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Dept. of Labor
Industrial air analysis

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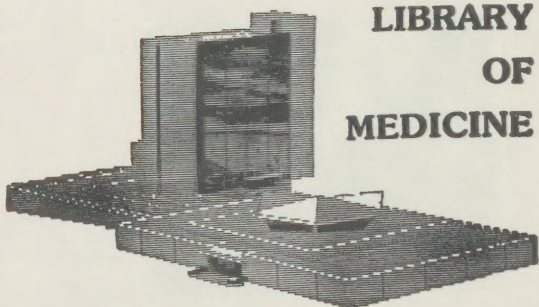
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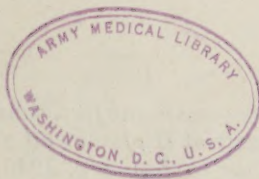
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New York (State) Division of
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INDUSTRIAL AIR ANALYSIS



New York State
Department of Labor
Division of Industrial Hygiene
and Safety Standards
80 Centre Street
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FOREWORD

A description of some of the chemical methods employed in the Laboratory of the Division of Industrial Hygiene, New York State Department of Labor were incorporated January 1, 1942, in a manual which has had a wide distribution. Because of a continuing demand for this material, a third revised edition has been prepared and is now available in mimeographed form for distribution, without charge to interested persons.

Some of the methods described herein are original contributions by staff members; some are modifications of methods originally described by others, or improvements designed to make them more applicable to the needs of field work.

The present issue is a reprint of the second edition to which has been added a method for the determination of organic vapors using a benzol indicator.

January 1, 1949

LEONARD GREENBURG, M.D.
Executive Director
Division of Industrial Hygiene

For additional articles on this subject, consult files of "Monthly Review", Division of Industrial Hygiene and Safety Standards, and "Industrial Bulletin" prior to January, 1946.

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I. INSTRUMENTAL METHODS

SAMUEL MOSKOWITZ, PH.D.

The industrial hygiene chemist is frequently called upon to estimate the concentration of contaminating fumes and vapors in air. This is done so that the industrial environment may be judged as to whether or not it is detrimental to the workers' health. The usual attack of the chemist is to absorb the contaminant in some suitable medium and then estimate the contaminant by quantitative chemical methods: gravimetric, volumetric, or colorimetric. In some few cases, a sample of the contaminated air itself is carried to the laboratory there to be analyzed for its content of foreign substance.

Within the past few years several instruments have been developed to supplement the activities of the chemist and to aid the industrial safety engineer in the determination of safe working conditions. One such instrument is the carbon monoxide (CO) indicator.

CARBON MONOXIDE INDICATOR

Carbon monoxide is a product of the incomplete combustion of carbon and of carbon compounds. It is a constituent of gas manufactured for industrial and home heating. The chemist has several methods for estimating the concentration of this toxic but odorless gas in air, but each of these is time consuming and so limits the number of specimens which he can take in any establishment in which a possible carbon monoxide hazard exists.

A portable instrument which permits almost innumerable tests to be made in a short space of time consists of a motor and pump to draw a stream of air, at a measured rate, through a Hopcalite catalyst. This catalyst permits the preferential burning of the carbon monoxide to carbon dioxide, the excess air supplying the necessary oxygen. The heat developed during this burning is directly proportional to the quantity of carbon monoxide burned. The increase in temperature due to the burning of the carbon monoxide is detected with a sensitive thermocouple which registers on a millivoltmeter which reads directly in hundredths of one per cent (parts per 10,000) of carbon monoxide in the air tested. The instrument is also supplied with a double scale galvanometer, the lower scale reading in thousandths of one per cent, for testing air with lower concentrations of carbon monoxide.

This instrument has been found very useful in the testing of motor truck and bus cabs, garages, automobile repair shops, gas fired equipment, and wherever incomplete combustion of carbonaceous fuels is suspected. The facts that the indicator is portable and gives an almost instantaneous reading of the carbon monoxide content of air are its chief advantages. The instrument must, however,

be calibrated against a standard chemical method for estimating carbon monoxide at various times during its use in order to insure a reasonable degree of accuracy.

COMBUSTIBLE GAS INDICATOR

Another portable instrument which is finding industrial use is the combustible gas indicator. This consists of a small vacuum tank whose pressure is kept below atmospheric by means of a hand operated aspirator bulb. Air to be tested is drawn over a heated platinum filament which is one arm of a Wheatstone bridge. Combustible gas in the air is burned on the surface of the platinum filament, raising its temperature and therefore, its electrical resistance. The increase in resistance depends upon the heat evolved during the burning and therefore on the concentration of combustible gas present. The change in electrical resistance unbalances the Wheatstone bridge and allows a flow of current to register on a galvanometer. The meter is calibrated to read directly in per cent of the lowest concentration of the combustible gas (in air) which will produce an explosion when ignited. Since a specimen of air to be tested may contain sufficient combustible gas to produce an explosion, the instrument is provided with flame arresters to prevent the setting off of the explosion by the heated filament. It has been found that a single meter calibration will suffice for all gases the product of whose molecular heat of combustion and the lower explosive limit concentration is a constant (1).

This instrument is most useful in testing air which contains a relatively high concentration of combustible vapors which are relatively non-toxic. Such conditions are found in mines where the chief contaminant is methane, and in tanks which had contained petroleum or petroleum distillates. Testing of the latter will indicate if it is safe for men to enter or if necessary welds may be made with safety. For use in mines, an instrument reading in terms of per cent methane in air is available.

With benzol as a contaminant in a workroom this instrument can serve only for exploration. The lower explosive limit concentration for benzol is 1.4 per cent. The lowest accurate reading on the combustible gas indicator is 2 per cent of that or about 300 parts per million. In concentrations of 100 parts per million in air, and perhaps even less, benzol is hazardous because of its toxicity. The standard combustible gas indicator is therefore, too insensitive to differentiate between a low but toxic and a non-toxic concentration of benzol vapor. Because of this, a special instrument has been developed for use with benzol. This instrument reads up to 1,000 parts per million of benzol in air, each scale division representing a concentration of 20 parts per million. It will, however, react to all other combustible vapors, and will give the true concentration of benzol only in the absence of other combustible vapors, but can also be used with proper calibration to estimate lower concentrations of combustible vapors than with the standard instrument.

INTERFEROMETER

The interferometer is a delicate optical instrument which can be used to compare the refractive indices of two specimens of gas or liquid. The refractive index of a medium is the reciprocal of the relative velocity with which light can pass through that medium, the speed of light through vacuum being taken as 1. The more concentrated a medium becomes the lower will be the speed of light through it and, therefore, the higher its refractive index. By comparing normal air with that encountered in an industrial environment, an estimate of its concentration of contaminants can be made. Unfortunately, not all impurities produce a marked change in the refractive index of air. Moreover, the instrument is non-specific: where several contaminants are present the reading obtained is due to the combined effects of all foreign substances. Nevertheless, the largest portable instrument, having a gas chamber 50 cm. long, is valuable in industrial hygiene surveys since readings can be made quite rapidly. A large factory can be investigated and places with the highest concentrations of contaminants studied more completely with chemical methods designed for that purpose.

OTHER INSTRUMENTS

Besides the instruments described above there are several small, inexpensive devices for the estimation of other impurities in air. One such is the hydrogen sulphide indicator. It consists of a hand operated aspirator bulb which draws a current of air to be tested through a glass capsule containing a chemical which becomes colored when it reacts with hydrogen sulphide. The degree of discoloration is a measure of the hydrogen sulphide content of the air. A carbon monoxide indicator much less sensitive than the one previously described and a cyanide detector operating on the same principle are also commercially procurable.

Instruments for the rapid estimation of foreign fumes and vapors in air are gaining in favor among industrial and safety engineers. Ease of operation and the rapidity with which results are obtained make these instruments convenient tools for those who try to maintain high safety standards on their premises. With proper regard for their limitations they may also be used by the chemist for more precise plant investigations.

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II. DETERMINATION OF ORGANIC VAPORS USING THE METHOD OF ADSORPTION

SAMUEL MOSKOWITZ, PH.D. AND WM. J. BURKE, CH.E.

Methods for the adsorption of solvent vapors on activated charcoal have been described by Fieldner and others (1), Greenburg (2), and more recently by Cook and Coleman (3). These consist essentially of drawing the air to be analyzed at a measured rate over substances for the purpose of removing moisture and carbon dioxide, and then through a tube of activated charcoal which has previously been heated, equilibrated with non-contaminated air, and weighed. After drawing a known volume of air through the gas chain, the charcoal tube is reweighed. The weight of substances adsorbed is the difference in weight. This can then be calculated to give the concentration of contaminants in terms of milligrams per liter, or if only one substance is present, in parts per million of air. The concentrations can be expressed in terms of parts per million even when several contaminants are present if the percentage by weight of each contaminant in the adsorbed vapor is known.

DIFFICULTIES ENCOUNTERED

In using the charcoal adsorption method, several difficulties have arisen. One of these was the difficulty of arriving at the weight of a glass tube filled with activated charcoal. Cook and Coleman report that the weight of a tube may be decreased by as much as 10 mg. by intensive wiping. This they attribute to additional moisture being removed from the glass, and recommend taking the weight of the tube exactly three minutes after the beginning of the wiping operation. We have found that the rate of change in weight at that time is so great that it is difficult to keep the balance in equilibrium in order to obtain an exact weight at the specified time. An error of several seconds in taking the weight may produce an appreciable change in the recorded weight. Moreover, we have found that the weight of a charcoal tube, whether taken three minutes after wiping is begun, or after allowing the tube to come to equilibrium with the laboratory air, will vary from day to day. We have been able to demonstrate a change in weight of as much as 21 mg. after a two day interval. During the same time a similar tube filled with Ascarite and Desicchlora showed a change of weight of only one mg. Changes in weight of charcoal filled tubes were not consistent or uniform, those which had adsorbed some organic vapor showing the most pronounced variations.

We have attributed the peculiarity in the action of the charcoal filled tube to a high static electrical charge which can be put on them by even gentle rubbing. Apparently each granule of carbon, especially when the surface is covered with adsorbed vapor with a

high dielectric, acts as an elementary electrical condenser. A high-frequency discharge (4) was not found effective in removing the static charge.

Another objection to the charcoal adsorption procedure is the time taken to prepare tubes of activated charcoal for field use. More than 24 hours may be required to equilibrate a tube with non-contaminated air.

DESCRIPTION OF APPARATUS

Silica gel has been used for the adsorption of paraffin hydrocarbon vapors (5) and for the adsorption of solvent vapors given off in spray painting (6), the latter with a rather complicated procedure which involves distilling the solvent away from the gel under reduced pressure, condensing, and weighing the condensate. We have found that tubes filled with silica gel, like those filled with Ascarite and Desicchlora, do not show the marked changes in weight on rubbing exhibited by charcoal filled tubes.



Figure 1.
Use of Silica Gel Adsorption Train in Field

Activated charcoal and silical gel as commercially prepared contain considerable quantities of adsorbed moisture and carbon dioxide. Instead of removing these substances by heating and equilibrating with dry, carbon dioxide-free air, we have introduced a weighed tube containing Ascarite and Desicchlora in the gas chain at a point immediately after the adsorption tubes. These retain the carbon dioxide and moisture lost by the adsorbant during a field test. The use of this tube removes the necessity of equilibrating the adsorbant tubes with non-contaminated air.

The adsorption train which we now use for field work (Figure 1) consists of five 150 mm. glass-stoppered Pyrex "U" tubes with one male and one female ground glass interchangeable connection on the side arms of each tube. The first tube contains a mixture of Ascarite (about 90%) and Desicchlora (about 10%) in the first limb and Desicchlora in the second limb. The second and third tubes are filled with eight to 16 mesh silica gel. The fourth tube is similar to tube number one and the fifth is also similar but reversed, that is, the Desicchlora is in the first limb. Each limb of each tube is topped with a plug of glass wool. No lubricant is used on the ground glass connections. We employ two tubes of silica gel because we have found that two tubes are necessary for efficient adsorption of organic vapors since silica gel is less efficient than an equal volume of activated charcoal for that purpose (7).

The function of the first tube is to remove water and carbon dioxide from the air to be tested. The two tubes of silica gel adsorb the organic vapors from the air. The fourth tube absorbs the carbon dioxide and water lost by the silica gel as the dry, carbon dioxide-free air passes over it. The last tube is a safety tube used to prevent the absorption of moisture and carbon dioxide if air should back into the train. The entire train is mounted on sponge rubber and is encased in wood for transportation in the field.

TESTING PROCEDURE

In making a test, the second, third and fourth tubes are rubbed well with a soft cotton cloth, allowed to come to equilibrium with the laboratory air, and weighed to constant weight. At the same time, another tube filled with either silica gel or Ascarite and Desicchlora is similarly treated. This tube is a blank. The train is assembled taken to the site of the test, and air at a rate of 20 liters per hour, is drawn through the train. A flowmeter is placed in the line between the train and the suction pump for the measurement of the volume of air sampled. The length of time during which the air is sampled depends on the concentration of contaminant expected. The usual sampling time is one to two hours.

On returning to the laboratory, a stopcock on each of the second and third tubes (each of which contains silica gel) and on the fourth tube (which contains Ascarite and Desicchlora) and on the blank is opened momentarily to permit equalization of pressure

to take place. The stopcocks are then closed and each tube is rubbed well, allowed to come to equilibrium with the laboratory air, and weighed to constant weight. If the blank tube has changed no more than one mg., no correction is used, otherwise the blank correction is applied to the weight of each of these tubes. The net change in weight of the three tubes in milligrams is divided by the volume of air in liters drawn through the train to give the concentration of contaminants in milligrams per liter of air.

If several successive tests are to be run, duplication of the three center tubes of the train is necessary. The initial tube will remove the water and carbon dioxide from a considerable volume of even very humid air before requiring refilling. The silica gel is replaced when it has adsorbed 10% of its weight of contaminants although commercial silica gel can be used beyond that without a breakdown (8).

USE OF APPARATUS

The adsorption apparatus has been found satisfactory for the estimation of aromatic and petroleum solvent vapors in atmosphere. It is the method of choice when a long continued air sample is desired for the determination of overall exposure to these air contaminants.

Where only a single contaminant is present in the air, its concentrations as milligrams per liter can be calculated in terms of parts per million of air or can be read directly as such from the table prepared by the United States Bureau of Mines (9). When several contaminants are present and rapid and complete evaporation of the solvent occurs, the concentration of each contaminant in the air will tend to be proportional to its concentration in the liquid evaporated. When, however, incomplete evaporation occurs, an approximation of the proportion in the air of each volatile constituent can be made by calculations from its vapor pressure and the effect on its vapor pressure of the other components.

Laboratory determinations with known amounts of solvents and using this system of adsorption have shown us that our maximum error is ± 3 mg. Taking a two hour sample (40 liters) and adsorbing a substance whose molecular weight is 100, the maximum error becomes less than 20 parts per million of air. The error may be reduced by using a longer sampling time.

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III. DETERMINATION OF ORGANIC VAPORS USING BENZOL DETECTOR

SAMUEL MOSKOWITZ, PH.D. AND WM. J. BURKE, CH.E.

One real advantage in using the benzol detector is the rapidity in which tests can be made to determine the concentrations of combustible solvent vapors in industrial atmospheres.

The instrument is especially useful for single spot test to determine a surge of vapors or for a series of spot tests to determine degree of variation of vapor concentrations.

TEST PROCEDURE

Instrument readings are made in the field with the drying cartridge removed from the instrument. A sample of the solvent or

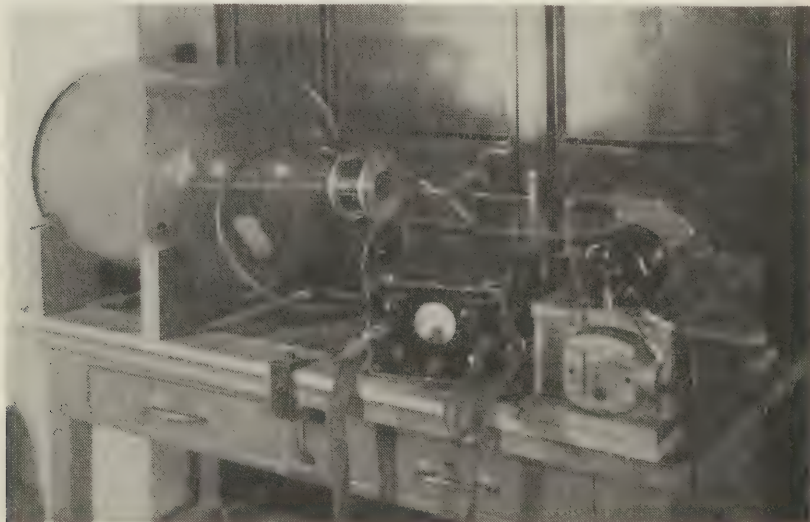


Figure 2.
Calibration of benzol detector (center foreground) for combustible solvent vapors.

solvent containing material whose vapors were tested is also obtained for chemical analysis. This sample is quantitatively analyzed in our laboratory by appropriate chemical and physical means to determine the composition of the solvent.

A measured portion of the solvent is also introduced into a glass U-tube attached to a large (52 liter) bottle. A small motor driven blower circulates air through a closed system which consists of the bottle, the U-tube and the blower. When the liquid in the U-tube has been completely evaporated and the vapor uniformly distributed through the air in the bottle, the benzol detector is attached to a tube leading into the bottle. This tube is opened and the air in the bottle is drawn through the benzol detector. The detector is read for the concentration of vapor which exists in the bottle. The detector is calibrated at several different vapor concentrations. Using this calibration, the concentrations encountered in the plant being investigated can be calculated.

This method of calibration of the benzol detector depends on uniform evaporation of the several volatile constituents which are usually present in a solvent. This does not usually occur because of differences in evaporation rate of various solvents. However, the error introduced by this approximation is minor and, on the whole, the method has been found highly satisfactory for the making of numerous vapor concentration determinations in a short time. The apparatus used in our Laboratory is illustrated in Figure II.

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IV. METHOD FOR ANALYSIS OF DUST AND FUMES FOR LEAD AND ZINC

SAMUEL MOSKOWITZ, PH.D. AND WM. J. BURKE, CH.E.

The use of lead-tin solder with zinc chloride flux is common practice in industries where soldering operations are carried out. In studying the atmospheric contaminants in plants using these materials it is desirable to have available methods for the determination of lead and zinc that are rapid, simple and accurate.

A review of available methods for the estimation of small amounts of these metals lead us to the conclusion that methods involving the use of diphenylthiocarbazone (dithizone) could satisfy these conditions (1), (2).

For lead, the dithizone methods are generally of three types: (a) The comparison of the intensity of color produced by the lead-dithizone complex with that produced with known amounts of

lead. Such a procedure has been described by Harrold, Meek and Holden (3). (b) The comparison of the mixed colors produced when a definite but excess of dithizone is added to lead-containing solutions (4), (5). (c) The titration of dithizone that had been combined with the lead against a lead standard (6).

The estimation of zinc with dithizone has been done colorimetrically and by the titration of the zinc-dithizone complex with bromine (7) and by titration of a zinc-containing solution with standardized dithizone, and indirectly by decomposing the zinc-dithizone complex with acid, adding an excess of silver nitrate and titrating the excess with standardized dithizone (8). The latter method is similar in principle to that employed by Winkler (9) for the determination of mercury.

All of the various colorimetric methods require the making of at least three comparison standards (since the color intensity is not proportional to the lead concentration), or the preparation of a calibration chart, or the use of some special optical instrument. When but a single sample is to be analyzed, these procedures become too time consuming. A critical examination of these methods lead us to the belief that the titrimetric method described by Horwitt and Cowgill (6) is most readily applicable to the solution of our problem. This method requires no special apparatus and requires the preparation of but a single standard. The titrimetric method was modified to eliminate reagents required particularly for the analysis of biological materials, and was simplified by using ordinary distilled water and ordinary C.P. chemicals without further purification.

A method for the estimation of zinc using the same principle as that for lead and removing the excess dithizone by the method described by Hibbard (7) has been developed in this laboratory. With this procedure the estimation of lead and zinc can be performed on a single sample of dust collected from air with only one standard for both determinations.

PREPARATION OF SAMPLE FOR ANALYSIS

The sample of fume or dust collected from the air is washed into a 250 or 400 cc. pyrex beaker with the aid of about 10 cc. of hot concentrated nitric acid. If the dust or fume is caught with an electrostatic precipitator, the aluminum tube may be washed down with hot 5% nitric acid, followed by hot distilled water. The contents of the beaker are evaporated just to dryness. Then 15 cc. of 1:1 hydrochloric acid is placed in the beaker and heated to boiling. This liquid is washed into a 100 cc. volumetric flask. To the beaker is then added 10 cc. of 20% sodium citrate solution and 3 cc. of 1:1 ammonia water. This is warmed and added to the volumetric flask. The beaker is then washed with two or three small portions of hot distilled water, the washings being also added to the contents of the volumetric flask. After cooling to room temperature, one cc. of 25% hydroxylamine hydrochloride solution and two drops

of phenol red are added. Using 1:1 ammonia water the pH is adjusted to about eight. The solution is again cooled to room temperature and made up to volume with distilled water. After thorough mixing to insure uniformity, aliquots are taken for the estimation of lead and of lead and zinc.

ANALYSIS

Reagents

- 1—HNO₃, conc.
- 2—HCl, 1:1.
- 3—HCl, 1%. Reagent 2, diluted 20 fold.
- 4—Ammonia water, 1:1.
- 5—Sodium citrate, 20%.
- 6—Ammonia water, dilute one cc. of Reagent 4, diluted to 250 cc.
- 7—Chloroform.
- 8—Hydroxylamine hydrochloride, 25%.
- 9—Dithizone solution. Dissolve (by trituration) 40 mgm. of diphenylthiocarbazone in 400 cc. of chloroform. Filter into a 500 cc. separatory funnel. Add 50 cc. of water and two cc. of Reagent 8. Shake well and keep in a cool, dark place. Draw off the reagent from the bottom of the funnel as it is needed.
- 10—KCN, 10%.
- 11—KCN, 0.5%. Reagent 10 is diluted 20 fold. Both Reagents 10 and 11 must be made fresh daily.
- 12—Phenol red, 0.04% in water.
- 13—Standard lead solution. Dissolve 1.599 gm. of pure, dry Pb (NO₃)₂ in water with the addition of one cc. conc. HNO₃. Make up to 100 cc. Dilute 10 cc. to 100 cc. and 10 cc. of this to 1,000 cc. Last solution contains 0.01 mg. Pb per cc. Keep this solution in a pyrex bottle. The dilute solution must not be more than five days old.

ESTIMATION OF LEAD

Extraction: An aliquot of the solution prepared for analysis is delivered by pipette into a 125 cc. Squibb separatory funnel. For ease of manipulation, the aliquot preferably should contain less than 50 micrograms of lead (one microgram = 0.001 mgm.). Then 0.5 cc. of 10% KCN and about 5 cc. of chloroform are added. The solution is diluted to 60 to 100 cc. and successive portions of about 0.5 cc. of dithizone solution are added with shaking between additions of the dithizone until the latter is present in excess. A rough estimate of the quantity of lead in the aliquot can be made by observing the volume of dithizone used to produce an excess. One cubic centimeter of dithizone will combine with approximately 40 micrograms of lead. The chloroform layer is withdrawn into another separatory funnel, and the aqueous phase is washed with about 2 cc. of chloroform and a few drops of dithizone.

Washing: The chloroform solutions are combined and washed at least twice by shaking with 1.5 volumes of 0.5% KCN each time. After each washing, the chloroform layer is removed and the aqueous solution is washed with about 2 cc. of chloroform and the chloroform solutions combined. The treatment with the 0.5% KCN removes the excess dithizone from the chloroform solution. If, however, a large excess of dithizone had been used, additional washings with KCN will be necessary. In any case, the washing must be continued until the aqueous solution is colorless instead of the brown which is the color of dithizone dissolved in aqueous potassium cyanide.

Titration: The chloroform solution now contains only the red lead-dithizone complex. This is shaken with two volumes of one per cent HCl. This treatment decomposes the complex, the lead entering the aqueous layer and the free dithizone which had been combined with the lead remaining in chloroform solution. The chloroform solution is drawn off, the aqueous layer washed with about 2 cc. of chloroform, and the chloroform solutions are combined. To the chloroform solution 0.5 volume of 0.5% KCN is added and the funnel is shaken. The dithizone distributes itself between the chloroform and aqueous layers, imparting a brown color to the latter. Dilute standard lead solution is added from a burette, about 0.1 cc. at a time, shaking between additions. The lead-dithizone complex enters the chloroform solution as it is formed. When sufficient lead to combine with most of the dithizone has been added, the aqueous solution will become almost colorless. The chloroform solution is then removed and discarded. The aqueous solution is washed with about 1 cc. of chloroform and 0.1 cc. of the standard lead solution. The chloroform is withdrawn and discarded. This is repeated until the chloroform no longer turns pink. The endpoint of the titration is the burette reading before the last addition of lead solution.

The number of cubic centimeters of lead solution used in the titration multiplied by 10 gives the quantity of lead, in micrograms, in the aliquot taken for analysis.

ESTIMATION OF ZINC

Extraction: A second aliquot of the solution which has been made up to a pH of about eight is placed in a 125 cc. Squibb separatory funnel. Preferably this should contain less than 25 micrograms of zinc or its equivalent of zinc and lead. In this case potassium cyanide is not added to this solution. Five cubic centimeters of chloroform and small portions of dithizone are added with shaking until the latter is present in slight excess. The chloroform layer is withdrawn and the aqueous layer is washed with a small portion of chloroform containing a few drops of dithizone. The two chloroform solutions are combined.

Washing: To remove the excess dithizone, the chloroform layer containing the lead and zinc-dithizone complexes is washed at least

twice with three volumes of dilute ammonia in each washing. Difficulty with emulsification will undoubtedly occur especially in the first washing. This may be overcome by allowing the emulsion to stand, drawing off the clear chloroform layer, and continuing this until the emulsion shows no signs of breaking further. A small portion of chloroform, about one cc., is then added, and the separatory funnel gently inverted several times. This will tend to collect the fine droplets. This should be repeated until the major portion of the chloroform extract has been removed. At this point, one or two cc. of chloroform may be added to the aqueous solution, shaken and allowed to settle. This is removed and added to the previous chloroform solution. It is inadvisable to wash the aqueous layer many times since dithizone distributes itself between chloroform and ammonia water. Too many washings may result in a large portion of the free dithizone which had been extracted being returned to the chloroform. Less trouble will be had with the second washing. As in the method for the estimation of lead the chloroform extract should be bright red and should show no sign of the presence of free dithizone. The last wash of ammonia water should be colorless.

Titration: The chloroform solution, which now contains both the lead and zinc is treated with two volumes of one per cent HCl. Violent and prolonged shaking will be required to break up the zinc and lead complexes. The dithizone-containing solution is withdrawn, treated with 0.5 volume of 0.5% KCN, and is titrated with the same standard lead solution as is used in the lead determination and in precisely the same way.

Subtracting the volume in cubic centimeters of lead solution used for titrating the lead contained in the aliquot taken for the zinc determination from the volume used for titrating the lead and zinc together, and multiplying this difference by 3.15 will give the quantity, in micrograms, of zinc present in the aliquot.

Blank determinations: These should be made to determine the lead and zinc content of the water and reagents used in the analyses. The blank values should be subtracted from those obtained in analyses of samples to obtain the corrected results.

LABORATORY ESTIMATIONS

Determinations on 31 solutions containing varying amounts of lead and zinc from 100 micrograms of lead and no zinc to 50 micrograms of zinc and no lead were made. These solutions were not evaporated to dryness with nitric acid as given in the section on preparation of the sample, but were introduced directly into separatory funnels for analysis. The results of these analyses are given in Table 1.

The results of the analyses reported in Table 1 show that estimations within ± 1 microgram of lead or of zinc can be made when the aliquot analyzed contains no more than 50 micrograms of lead or of zinc. The blank values used are one microgram for lead and five micrograms for zinc.

TABLE 1

| Taken | | Results | | | | Error | |
|-------|-------|---------|-------|---------------------|-------|-------|-------|
| | | Found | | Corrected for blank | | | |
| Pb | Zn | Pb | Zn | Pb | Zn | Pb | Zn |
| Micro | grams | Micro | grams | Micro | grams | Micro | grams |
| 0 | 0 | 1 | 5 | | | | |
| 0 | 0 | 1 | 4 | | | | |
| 1 | 0 | 2 | 6 | 1 | 1 | 0 | +1 |
| 2 | 0 | 3 | 5 | 2 | 0 | 0 | 0 |
| 5 | 0 | 6 | 6 | 5 | 1 | 0 | +1 |
| 10 | 0 | 10 | 6 | 9 | 1 | -1 | +1 |
| 20 | 0 | 20 | 4 | 19 | -1 | -1 | -1 |
| 50 | 0 | 51 | 5 | 50 | 0 | 0 | 0 |
| 100 | 0 | 99 | 6 | 98 | 1 | -2 | +1 |
| 0 | 5 | 1 | 10 | 0 | 5 | 0 | 0 |
| 1 | 5 | 2 | 9 | 1 | 4 | 0 | -1 |
| 2 | 5 | 3 | 10 | 2 | 5 | 0 | 0 |
| 5 | 5 | 7 | 9 | 6 | 4 | +1 | -1 |
| 10 | 5 | 10 | 10 | 9 | 5 | -1 | 0 |
| 20 | 5 | 20 | 9 | 19 | 4 | -1 | -1 |
| 50 | 5 | 50 | 11 | 49 | 6 | -1 | +1 |
| 0 | 10 | 1 | 16 | 0 | 11 | 0 | +1 |
| 1 | 10 | 2 | 15 | 1 | 10 | 0 | 0 |
| 2 | 10 | 3 | 15 | 2 | 10 | 0 | 0 |
| 5 | 10 | 5 | 15 | 4 | 10 | -1 | 0 |
| 10 | 10 | 10 | 14 | 9 | 9 | -1 | -1 |
| 20 | 10 | 20 | 15 | 19 | 10 | -1 | 0 |
| 50 | 10 | 50 | 16 | 49 | 11 | -1 | +1 |
| 0 | 20 | 1 | 24 | 0 | 19 | 0 | -1 |
| 1 | 20 | 2 | 25 | 1 | 20 | 0 | 0 |
| 2 | 20 | 3 | 25 | 2 | 20 | 0 | 0 |
| 5 | 20 | 5 | 25 | 4 | 20 | -1 | 0 |
| 10 | 20 | 10 | 24 | 9 | 19 | -1 | -1 |
| 20 | 20 | 21 | 24 | 20 | 19 | 0 | -1 |
| 50 | 20 | 50 | 25 | 49 | 20 | -1 | 0 |
| 0 | 50 | 1 | 55 | 0 | 50 | 0 | 0 |

To test the first part of the procedure—the preparation of the sample for analysis as described above—three samples were made and evaporated to dryness with nitric acid. These samples were prepared so as to contain:

- I— 50 micrograms lead and 120 micrograms zinc.
- II—100 micrograms lead and 100 micrograms zinc.
- III— 50 micrograms lead and 20 micrograms zinc.

After evaporation to dryness, they were taken up with hydrochloric acid, and the remainder of the procedure followed as previously outlined. Aliquots, not the same volume in each case, were

taken and analyzed for lead and zinc. The blanks used for correcting the results are one microgram for lead and five micrograms for zinc. The results of these analyses are presented in Table 2.

The results of the analyses reported in Table 2 indicate that the initial evaporation of the sample and its subsequent preparation for analysis do not lower the accuracy of the method.

TABLE 2

| Sample | Aliquots taken to contain | | Found (corrected for blank) | | Error | |
|--------|---------------------------|-------|-----------------------------|-------|-------|-------|
| | Pb | Zn | Pb | Zn | Pb | Zn |
| | Micro | grams | Micro | grams | Micro | grams |
| I | 30 | 36 | 30 | 37 | 0 | +1 |
| II | 30 | 20 | 30 | 21 | 0 | +1 |
| III | 20 | 10 | 21 | 11 | +1 | +1 |

INTERFERENCE BY OTHER METALS

Bismuth and tin: Bismuth and stannous tin give complexes with dithizone similar to that given by lead in the presence of cyanide. The initial evaporation with nitric acid converts tin to the stannic state in which form it does not interfere with the lead analysis. Bismuth is not commonly encountered in industrial fumes except where low melting alloys are processed. Unless much bismuth is present with the lead, it will be extracted during the washing with potassium cyanide.

Copper: In the absence of cyanide, copper will be extracted with dithizone along with lead and zinc. Since soldering operations commonly involve the heating of copper or copper alloys, a procedure was evolved to eliminate interference by this metal when it is present.

When the alkaline solution that has been prepared for analysis is extracted with dithizone in the absence of cyanide, the chloroform solution will contain the lead, zinc, and copper-dithizone complexes and an excess of free dithizone. Unless an estimation of the copper present is to be made, the extract is not washed with ammonia water. The chloroform solution is shaken with two different portions of one per cent HCl, each twice the volume of the chloroform. If a copper determination is to be made, the chloroform layer is kept; if not, it is discarded. The acid solution is brought to a pH of about eight with 1:1 ammonia water, using phenol red as the indicator. The lead, zinc, and residual copper is again extracted with an excess of dithizone and the chloroform

solution again treated with hydrochloric acid. The acid solution is once more brought to a pH of about eight with ammonia water and finally extracted with dithizone in excess. The excess is washed out with dilute ammonia, the lead and zinc complexes decomposed with hydrochloric acid, and the liberated dithizone titrated with the standard lead solution in the presence of potassium cyanide.

Using this procedure the results given in Table 3 were obtained.

Hibbard (7) recommends a single treatment with 0.5 N hydrochloric acid for the separation of copper and zinc. Using the somewhat more dilute (one per cent) hydrochloric acid, we found that the copper-dithizone complex is decomposed to some extent when it is present in large quantities. With sample A, eight micrograms of copper was found in the first hydrochloric acid wash. This was completely eliminated with the second treatment. Lead and zinc remain together during these operations so that this treatment is used to determine the lead and zinc as a total.

If copper is to be determined, the initial extract of lead, zinc, and copper-dithizone complexes is washed with dilute ammonia to remove the excess free dithizone. After treating with one per cent HCl, the aqueous solution is retained for further treatment and used for the estimation of lead and zinc together as described above. The chloroform solution is shaken with 0.5 volume of 0.5% KCN and titrated with the standard lead solution. It is unnecessary to have the copper-dithizone complex decomposed by acid as the addition of potassium cyanide will release the dithizone from the complex for titration with lead. The difference between the volume of lead solution used in this titration and that used for the titration of lead and zinc together multiplied by 3.07 gives the quantity of copper, in micrograms, present in the aliquot.

TABLE 3

| Sample | Taken | | Results | | Error |
|--------|-------------|----|-------------|---------------------|------------|
| | | | Found | Corrected for blank | |
| | Zn | Cu | Zn | Zn | Zn |
| | Micro grams | | Micro grams | | Micrograms |
| A | 0 | 50 | 4 | Blank | |
| B | 20 | 0 | 25 | 20 | 0 |
| C | 20 | 10 | 24 | 19 | -1 |
| D | 20 | 50 | 25 | 20 | 0 |

TABLE 4

| Sample | Volume of air samples | Concentration found in air | |
|--------|--------------------------|----------------------------|--------|
| | | Pb | Zn |
| | cu. ft. | mgm. /10 | cu. m. |
| 1 | 85 | 0.97 | 12.3 |
| 2 | 62 | 0.53 | 5.1 |
| 3 | 42 | 0.45 | 7.6 |
| 4 | 37 | 1.03 | 4.3 |
| 5 | 71 | 1.65 | 2.0 |
| 6 | 71 | 1.20 | 2.9 |
| 7 | 71 | 0.42 | 6.7 |

APPLICATION OF THE METHOD

Table 4 gives typical results of air tests made in a factory in which soldering of copper and brass with a lead-tin solder using a flux containing zinc and ammonium chlorides is done.

No appreciable quantity of copper was found present in these air samples. Where brass is melted, as in foundries, there may be copper, zinc, and lead fumes present. The use of the procedure described for eliminating the interference by copper will then be necessary.

Taking air samples as small as one cubic meter (35.3 cubic foot) and using an aliquot representing 50% of the fume collected, an accuracy of 0.02 mgm. per 10 cubic meter can be obtained in the analytical procedure. The accuracy of sampling by most procedures is probably much lower than that obtainable in the analytical procedure. The use of all pyrex glassware and purified water and reagents could undoubtedly increase the accuracy of the chemical analysis, but in view of the inherent errors of sampling, it is unnecessary to use a more refined analytical procedure, as more exact figures in the result would actually be without significance.

SUMMARY

1. A titrimetric method for the estimation of lead, zinc, and copper, in samples of dust and fumes collected from the air is described.

2. This method consists in the extraction of the metal as a dithizone complex, removing the excess dithizone reagent, decomposing the complex, and titrating the liberated dithizone against a standard lead nitrate solution.

3. Analyses of solutions with known amounts of lead and zinc disclose the accuracy and precision of the method to be 0.001 mgm. when less than 0.050 mgm. of these metals is present in the original sample.

4. The application of the method to industry is indicated.

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V. A MODIFIED METHOD FOR THE DETERMINATION OF BENZOL IN AIR

JAC SIEGEL, B.S. AND WM. J. BURKE, CH.E.

During the course of an investigation of acute benzol poisoning in three rotogravure printing plants in New York City, it was found necessary to collect and analyze large numbers of air samples for the estimation of benzol concentrations in the air. In order to meet this need, a modification was developed of the microcolorimetric method developed at the Bureau of Mines by Schrenk, Pearce and Yant which proved very helpful to us. This modification is being reported for the benefit of other workers in the field who may be faced with a similar situation.

In the method described by Schrenk and his co-workers, (1) alternative procedures are given for the collection of air samples. First, a measured amount of air may be slowly drawn into a bubbler tube containing a nitrating mixture of fuming nitric and concentrated sulfuric acids. In their alternate procedure, a sample of air may be taken in a gas collection bottle, returned to the laboratory, and then drawn through a nitrating bubbler at a very slow rate (about 20 to 30 ml. per minute). Both these procedures were found to be impracticable in the handling of a large number of samples because they were time consuming, and hence materially limited the number of samples that could be handled in a day.

METHOD MODIFIED

In our study the following modification of the Schrenk, et. al. method was found to work satisfactorily and to be well adapted to

our problem. Samples of air were taken in separatory funnels, ranging in size from 100 to 800 ml. The selection of funnel size depended on the height of concentration expected, e.g., the greater the expected concentration the smaller the funnel used, and vice versa. Previous to their use, the funnels were thoroughly degreased, and the stopcock and stopper were lubricated with graphite.

The air was drawn into the separatory funnel by means of a hand pump. Sufficient air was pumped through the funnel to insure proper sampling of the air. The closed separatory funnel with the air sample was then returned to the laboratory. All of the subsequent operations were conducted in the same separatory funnel, thereby eliminating any error introduced by transfer of material as required in the Bureau of Mines method.

In our method, the separatory funnel containing the air sample was cooled and two cc. of the nitrating mixture was introduced into the funnel through its stem. After closing the stopcock, the interior of the separatory funnel was wetted by rotation and it was permitted to remain on its side overnight. In the morning the funnel was immersed in a beaker of ice water, the sample was diluted with five cc. of water and then neutralized with 40% sodium hydroxide. A slight excess of the sodium hydroxide was added, followed by 10 cc. of ethyl methyl ketone. The contents of the flask were shaken and after complete separation the aqueous layer was drawn off and discarded. The ethyl methyl ketone layer was then run into a 50 cc. Nessler comparison tube and 1.5 cc. of 40% sodium hydroxide was added. The comparison was then made following the method of Schrenk and his colleagues.

Taking an air sample of 100 cc., the estimation of benzol in air can be made with an error not exceeding 10 p.p.m. Taking samples of larger volumes the error can be reduced proportionally.

As pointed out previously, it was necessary in our study to determine benzol concentration in a large series of samples. By using this method, 15 to 20 samples could be analyzed simultaneously. Furthermore, with this procedure, high surges in concentration or the existence of dangerous pockets could be readily detected. The detection of these high concentrations indicated where improvement in the existing ventilation system was required, or where additional units were necessary.

A similar modification has been found applicable to the Bureau of Mines method for the estimation of toluol in air (2).

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VI. ESTIMATION OF MERCURY IN AIR

WM. J. BURKE, CH.E., SAMUEL MOSKOWITZ, PH.D.
AND B. H. DOLIN, M.A.

Mercury is one of the toxic heavy metals which is rather frequently encountered in industry. The metal itself or its compounds are found in such varied industries as the manufacture of amalgams, felt hats, explosives, pharmaceuticals, scientific instruments such as thermometers and barometers, electrical apparatus, synthetic chemicals and dyestuffs, electrolytic products such as lye and chlorine, paints, and mirrors. In addition, workers engaged in or about plants using mercury boilers, in laboratories or in factories engaged in the metallurgy of mercury or of gold, may be exposed to mercury in their industrial environment.

Mercury is the only metallic element which is liquid at ordinary temperatures. Some of its uses depend on that property. The boiling point of mercury is rather low, 357° C. or 675° F. At this temperature the vapor pressure is 760 mm. The vapor pressure decreases rapidly with a decrease in temperature but even at room temperatures the vapor pressure is appreciable. At 20° C. (68° F.) the vapor pressure is 0.001201 mm. of mercury (1). One cubic meter of air saturated with mercury vapor at this temperature contains 13 mg. of the metal. This is considerably higher than the concentration generally considered safe for prolonged exposure. In industry, dirt and grease frequently cover any mercury which might be spilled. Dirt and grease hamper the evaporation of the metal. Nevertheless, the exposure of the metal to the air may produce a hazardous concentration of this substance in the air to which employees are exposed.

Mercury in the form of its compounds may be dispersed through air in the form of a fine dust, or it may be present as a compound adhering to some other air-floated material. This is especially true in the felt hat industry and in the preparation of hair for the manufacture of felt hats. In these industries fine hairs containing mercuric nitrate are blown about through the atmosphere. These may be inhaled by workers and prove to be injurious.

The estimation of the concentration of mercury, in free form and in the form of its compounds, is a necessary procedure in evaluating the degree of toxicity of the air in an industry in which mercury is used or present.

MERCURY VAPORS

Mercury vapor in air may be caught by condensing the mercury by passing the air through a tube immersed in liquid air or cooled with solid carbon dioxide. The mercury is then estimated by depositing the metal electrolytically on gold foil and weighing on a microbalance, or by collecting the mercury in a single droplet and measuring its diameter microscopically (2).

A more convenient method for the estimation of mercury vapor in air is the apparatus devised by Nordlander (3). This instrument (Figure 3) contains a fan and motor used for drawing filtered air at a measured rate through a heated chamber. The air, heated to a temperature of 70°C ., is allowed to impinge on a strip of paper coated with selenium sulphide. The darkening of the paper, caused by the formation of black mercuric sulphide, is a function of the quantity of mercury in the air sampled for analysis. While any metal giving a black or dark brown sulphide will affect selenium sulphide paper similarly, actually, none other than mercury is sufficiently volatile at room temperatures to give any appreciable discoloration even after many hours of exposure.



Figure 3.
Nordlander apparatus for the estimation of mercury vapor in air.

By comparison with a series of standard papers the concentration of mercury vapor to as low as 10 parts per billion by volume, approximately 0.08 mg. per cubic meter, in the air may be determined by direct reading.

Another, more recently developed, mercury detector depends on the scattering of the resonance radiation of mercury (ultra violet light with a wave length of 2,537 Angstrom units) by mercury vapor (4). The degree of opaqueness to light of this wave length of the air tested is a measure of the concentration of mercury vapor in the air. The estimation is made photoelectrically and gives a rapid reading of the mercury vapor content of air even

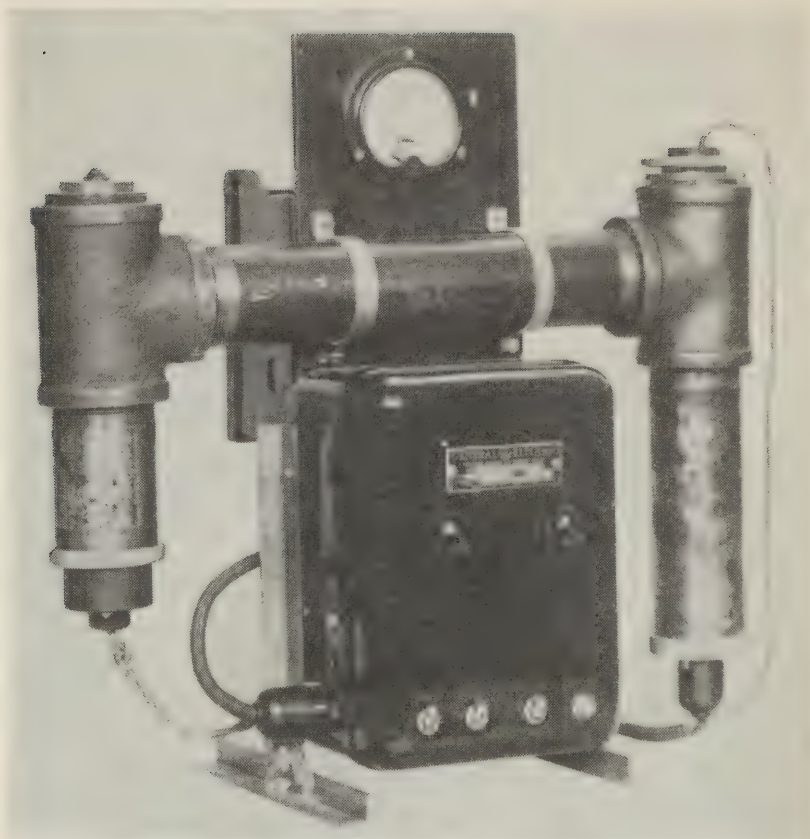


Figure 4.
Laboratory model of Woodson apparatus for the estimation of mercury vapor in air.

to as low a concentration as one part per billion. Figure 4 shows a laboratory model of this instrument. This is an improvement over the Nordlander method since the latter apparatus will require several hours for an estimation when the mercury content of the air tested is low. This instrument is now commercially available in portable form.

A similar instrument, designed to measure the concentration of certain organic vapors in air, can also be used for the estimation of mercury vapor in air (5).

MERCURY IN DUST

Mercury may be distributed in air in the form of dust. This dust can consist of mercury compounds or of some substance to which metallic mercury or a compound of mercury is adhering. To estimate the mercury content of the dust in air, the dust is

caught and collected by means of a Greenburg-Smith impinger or other satisfactory dust collector. If an impinger is used, the flask contains water or, if the dust is greasy, water and alcohol. Sufficient sample is collected to give the quantity of mercury required for an accurate analysis.

The collected dust is put into solution by appropriate methods. If the dust is organic, it is digested with nitric and sulphuric acids and potassium permanganate. To avoid loss of mercury by evaporation, a reflux condenser must be used whenever mercury-containing solutions are boiled. The mercury present in solution may then be estimated electrolytically (6). If this method of analysis is used, sufficient dust should be collected to contain at least 0.3 mg. of mercury in order to insure an accurate estimate of the mercury contained in the sample.

Modifications of Winkler's dithizone method for mercury (7) have been used for the estimation of mercury in biological materials (8), (9), and by the Division of Industrial Hygiene for the estimation of this metal in air-borne dust and also in urine. An accuracy and precision of 0.005 mg. of mercury is readily obtained with this method so that the quantity of sample required for an accurate analysis may be reduced to one containing as little as 0.05 mg. of mercury. The method employed here is described below.

The sample of dust collected and washings from the collector are digested under a reflux condenser with about 25 cc. of concentrated nitric acid, 2 cc. of concentrated sulphuric acid, and sufficient potassium permanganate until the organic matter is completely destroyed. More permanganate and nitric acid may be added if necessary. The manganese dioxide and excess permanganate are removed by the dropwise addition of superoxol (30% hydrogen peroxide). The dissolved oxygen is expelled by boiling. After cooling, about one-half gram of hydroxylamine hydrochloride is added, and the solution is extracted by shaking with successive portions of a chloroform solution of dithizone (diphenylthiocarbazone), containing 25 mg. per liter, until it is present in excess. Dithizone solution is green; its complex with mercury is orange.

The chloroform extract is treated with 50 cc. of water at 50-60° C., 2 cc. of five percent potassium permanganate solution, and 2 cc. of 1:1 sulphuric acid. The mercury passes into the aqueous solution. The chloroform is withdrawn and discarded. To the aqueous solution is added sufficient 10% sodium or potassium nitrate solution to react with the excess permanganate. The free nitrous acid left in solution is destroyed by adding about one-half gram of hydroxylamine hydrochloride and heating just to boiling.

If large amounts of copper are present, the mercury may be inactivated by the addition of iodide ion. On reextracting with dithizone the copper is removed and the mercury is left in the aqueous solution. After the excess iodide is destroyed or the solu-

tion made ammoniacal, the mercury may be estimated by the titration procedure described below. Small amounts of copper will not interfere with the analysis for mercury since only a small percentage of the copper present will be extracted with dithizone from a solution sufficiently acid (pH 2) to permit extraction of the mercury present (10).

The cooled solution is titrated in a separatory funnel with a carbon tetrachloride solution of dithizone containing about 12.5 mg. per liter. This is added, a small portion at a time with shaking, until it is present in excess. Standard mercuric nitrate solution containing exactly 10 mg. of mercury per liter is used for the back titration of the excess. The titre of the dithizone solution is determined each day it is used by treating a solution containing 0.1 mg. of mercury as mercuric nitrate in the same manner as described for an unknown sample. All the reagents used must be as pure as it is possible to procure them, and blank determination on water alone must be performed to determine the mercury content of the water and reagents used in the analytical procedure. The content of mercury in the reagents must be subtracted from that found in a sample to determine the quantity actually present in the material analyzed.

Analysis of industrial air for its content of mercury vapor, and of mercury in the form of dust, if both are present, will give the total concentration of this metal in air to which workers are exposed.

We wish to thank the General Electric Co. for furnishing the photographs used in this article. (Figures 3 and 4)

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VII. ABSORPTION OF GASES IN LIQUIDS

SAMUEL MOSKOWITZ, CH.E., JAC SIEGEL, B.S.
AND WM. J. BURKE, CH.E.

In a previous article in this series (1) general methods for the estimation of contaminants in industrial air were discussed. It was then stated that the usual approach by the chemist is to absorb the contaminant in some suitable medium and then estimate the absorbed substance by suitable quantitative chemical methods: gravimetric, volumetric, or colorimetric. Chemical methods for the estimation of the toxic substances usually encountered in industrial air have been described (2), but there has been little agreement among industrial hygienists as to apparatus for the collection of those air-borne materials which are best absorbed in liquids.

Gas-washing bottles of the Drexel, Friedrichs, and Milligan types have been used for many years both for the drying and for the absorption of gases. More recently, the use of sintered glass disks has added a new type of gas-washing bottle. Prausnitz in 1932 (3) listed a bibliography on the use of sintered glass gas-washing bottles in gas analysis. In this type of absorber the bubbles of gas entering the liquid are much smaller than in the older types. The length of travel of these bubbles is, however, no greater than that in the Drexel type and therefore, much less than in the spiral types.

The Drexel bottle is much less efficient than the Friedrichs spiral type, while the sintered glass and the Friedrichs bottles have about the same efficiencies (4). Several variations of the spiral type washing bottle with greater efficiencies than those of the more conventional types, have been described (5). The sintered glass absorber can, however, handle a faster stream of gas and maintain its high efficiency without any large increase in resistance in the gas flow (6). This feature is especially important where the concentration of the gas to be absorbed is low.

Despite the choice of gas-washing bottles which have been described above, special gas absorbers have been devised for specific estimations of toxic contaminants in industrial air, such as in the estimation of nitric oxide (7), benzol (8), phosgene (9), chlorinated hydrocarbons (10), (11), and other gases.

APPARATUS USED IN THIS LABORATORY

While several of the special absorbers for specific contaminants are being used in this laboratory, it has been found that most of the sampling requiring absorption of gases in liquids could be done with one type of apparatus. It was deemed advisable, however, from considerations of ruggedness and economy, to standardize on two types of apparatus.

The first apparatus consists of a 250 cc. glass-stoppered Drexel wash bottle with standard taper ground glass connections at the entrance and exit tubes, equipped with glass hooks sealed at the connections as an aid in keeping joints tight when several bottles are used in series. A sintered glass disk with No. 1 porosity (German designation) is fused to the end of the gas entrance tube near the bottom of the bottle.¹ About 100 cc. of absorbing liquid is used in each bottle. (Figure 5) Two or more such bottles can be connected in series without the use of any rubber because of the ground glass connectors. This apparatus is used for those estimations in which contact between the air to be analyzed, or the medium used for absorption and rubber, metal, or cementing materials is to be avoided. The disadvantages of this absorption apparatus are the cost, which is high, and lack of flexibility because of its all-glass connections.

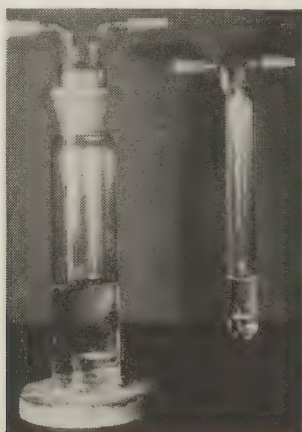


Figure 5.
Large and Small All-Glass Absorbers

For use with small volumes of liquids, this type of apparatus has been made in one piece about seven inches high by one inch outside diameter. The ground glass connections at the ends of the gas entrance and exit tubes are interchangeable but smaller than those on the larger apparatus. Since the sintered glass disk is smaller in diameter, it is advisable to reduce the rate of gas flow through this absorber to about two-thirds that through the larger apparatus. From 10 to 15 cc. of absorbing liquid is sufficient in an absorber of this type. (Figure 5)

¹ The sintered glass gas dispersion disks may be made in the laboratory (12) and are now also manufactured in this country (13). Porosity B in those disks manufactured here most nearly correspond with No. 1 in those of foreign make. These disks are now also made by the Corning Glass Works. Their designation for the porosity used by us is C (14).

The second apparatus consists of a glass vial about $4\frac{1}{2}$ inches high by $1\frac{3}{4}$ inches outside diameter. This is fitted with a two-hole rubber stopper. The gas entrance tube extends nearly to the bottom and ends in an Aloxite stone² attached by means of some cement or by a rubber connection fitting over the metal nipple with which some of these stones are supplied. About 35 cc. of absorbing liquid is placed in each vial. (Figure 6) As many of these as are necessary are connected in series. This apparatus is very cheap to construct and has the additional advantage of flexibility of connection between absorbers. This apparatus is used in all cases except where the presence of rubber, metal, or cementing material interferes with the analysis.

A modification of this type, which eliminates the presence of rubber and metal, consists of a Drexel bottle with an Aloxite stone cemented to the inner end of the gas entrance tube. If ground glass

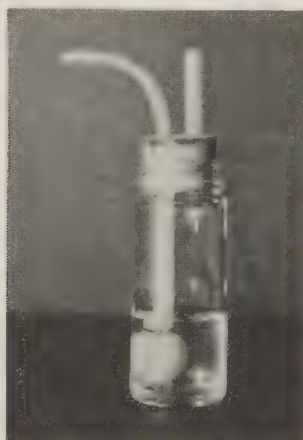


Figure 6.
Absorber with Aloxite Gas Distributor

connectors are not sealed at the outer ends of the entrance and exit tubes, interference by rubber can be largely eliminated by carefully squaring the ends of the glass tubes and connecting them with a piece of rubber tubing which permits a glass to glass contact. The cementing material alone must then be selected so that it will cause no interference with the absorption and analysis. Litharge and glycerine, magnesium oxychloride, and bakelite resin are a few of the cements which may be employed for this purpose. This apparatus is cheaper and enjoys most of the advantages of the all glass apparatus.

In using these pieces of equipment for the absorption of gases from industrial air, it has been found necessary to use only two

² Manufactured by the Carborundum Co., Niagara Falls, New York.

absorbers in series when the air is run through at a rate of 30 liters per hour. The length of time required for sampling depends on the concentration of contaminants encountered and on the precision and accuracy of the chemical analytical method. The usual sampling time varies from 20 minutes to two hours. With the all glass apparatus, an all glass flowmeter with a ground glass joint to fit those of the washing bottles may be used on the downstream side; any flowmeter connected with rubber tubing may be used on the upstream side. In the latter case, the flowmeter must be calibrated to read in terms of flow of air at atmospheric pressure although at that point the gas passing through the flowmeter is at a pressure somewhat below atmospheric. The drop in pressure through each sintered glass disk is about inch inch of mercury when the air rate of flow is 30 liters per hour. The second type of absorption apparatus using Aloxite aeration stones is used with a flowmeter on the downstream side. The drop in pressure across each stone is about 3 inches of mercury with an air flow of 30 liters per hour.

A case in which as many as five all glass absorbers in series can be carried and used in the field has been constructed for us. One end of the case holds a differential flowmeter which has been calibrated to read in terms of flow of air at atmospheric pressure when from one to five of the absorbers are on the downstream side. Similarly, we have a block in which we can insert one or more of the vials containing Aloxite stone gas distributors. A flowmeter is attached for use on the upstream side.

The all glass apparatus is used for the estimation of hydrogen sulphide, carbon disulphide, these two gases simultaneously, acid vapors and mist, and ammonia. The apparatus containing the Aloxite stone gas disperser is used for the estimation in air of methanol and other alcohols, formaldehyde and other aldehydes, and phenols. While the lists given are not complete, they represent those contaminants which we are most frequently called upon to determine and which require absorption of the gas in a liquid medium.

Complete directions for carrying out one analysis using each type of apparatus by the methods used in the Laboratory of the Division of Industrial Hygiene are given below.

SIMULTANEOUS ESTIMATION OF HYDROGEN SULPHIDE AND CARBON DISULPHIDE IN AIR

Apparatus: Five all glass absorbers in series.

The first three absorbers contain 100 cc. each of cadmium chloride solution (20 grams dissolved in 900 cc. water to which is added 20 cc. of 0.5 N sodium hydroxide). The last two absorbers contain 100 cc. each of 0.1 N potassium hydroxide in anhydrous ethyl alcohol.

Air is drawn through the train at the rate of 30 liters per hour for about one hour. At the end of the sampling time, uncontaminated air is drawn through for an additional five minutes to prevent any possible entrainment of carbon disulphide in the first three bottles.

Hydrogen sulphide: The contents of the first two absorbers are transferred to a glass stoppered Erlenmeyer flask. The contents of the third are also used if the concentration of hydrogen sulphide is high. The absorbers are first rinsed with water then with concentrated hydrochloric acid using 25 cc. for each 100 cc. of absorbent and water rinse collected in the flask. The rinsings are combined in the flask. Then 25 cc. of 0.005 N iodine solution are rapidly added and the excess iodine is titrated with 0.005 N sodium thiosulphate solution. Starch is used as an indicator to reach the approximate endpoint. The titration is continued until no color remains in a small volume of chloroform (about 5 cc.) when shaken with the solution being titrated.

The sodium thiosulphate is standardized against standard potassium dichromate solution and the iodine is standardized against the sodium thiosulphate. Blanks must be run on the reagents alone and this value allowed for in calculating the hydrogen sulphide present.

Calculation: One cc. of 0.05 N iodine is equivalent to 0.0846 mg. of H_2S . This quantity of H_2S in 30 liters of air represents 2.0 parts per million of air by volume at 25° C. and one atmosphere pressure.

The overall accuracy of the estimation is about 0.5 p.p.m. when testing air whose concentration of hydrogen sulphide is within the range of hygienic significance and a 30 liter sample of the air is taken.

Carbon disulphide: The contents of each of the last two absorbers is made up to 100 cc. with alcohol. An aliquot of 40 cc. (less if found necessary) is withdrawn from each and placed in separate 50 cc. Nessler comparator tubes. To each is added 2 drops of phenolphthalein, sufficient acetic acid to make faintly acid, and 4 drops of 0.5 percent cupric acetate. The contents of the tubes are mixed and the volume made up to the 50 cc. mark with alcohol. Simultaneously, a series of standards are made up by adding from 0.1 cc. to 1.0 cc. of a solution of carbon disulphide in alcohol containing 0.25 mg. CS_2 per cc. to 40 cc. of alcoholic potassium hydroxide (0.1 N). Each of these tubes is similarly treated with acetic acid and cupric acetate. The yellow color of copper ethyl xanthate of the unknowns is compared with standards having the closest match in color intensity; a colorimeter is used for more precise results.

Calculation: 1.0 mg. CS_2 is equivalent to 10.6 p.p.m. of air if 30 liters of air are sampled.

The accuracy of the absorption and estimation is within 0.5 p.p.m. of air if 30 liters of air containing a concentration of carbon disulphide of hygienic significance are sampled.

ESTIMATION OF FORMALDEHYDE IN AIR

The apparatus used for this determination consists of two vials fitted with Aloxite stone connected in series. Each vial contains about 35 cc. of water. A flowmeter on the downstream side is used to control the rate of air flow which should be 30 liters per hour. Sampling for one hour is usually sufficient for a determination. If the samples are not to be analyzed within 24 hours, sufficient aldehyde-free ethyl alcohol is added to make the alcohol concentration about 10% by volume. Commercial anhydrous alcohol without further purification has been found satisfactory for this purpose.

The samples and rinsings from the vials are made up to 50 cc. each with water and are cooled in a refrigerator before the analysis. The reagents employed in the analysis are also cooled before used. A 25 cc. (or smaller, if necessary) aliquot of each is transferred to 50 cc. Nessler comparator tubes. To each is added 4 cc. of 1% phenylhydrazine hydrochloride and 2 cc. of 5% potassium ferri-cyanide. These two reagents should be made up the day they are to be used. To each tube is then added 8 cc. of concentrated hydrochloric acid, the contents of each tube mixed, and the volume made up to 50 cc. with water. Standards made up to contain 0.02 to 0.5 mg. of formaldehyde are treated similarly. The tubes containing the standards and unknowns are placed in the refrigerator for ten minutes in which time a red-violet color develops. The color intensity of the unknown is read in a colorimeter against the standard showing the closest match, and the amount of formaldehyde collected in each vial calculated.

Calculation: 1.0 mg. of formaldehyde in 30 liters of air is equivalent to a concentration of 27 p.p.m. by volume.

The overall accuracy of this method for the collection and estimation of formaldehyde in air when it is present in concentrations of hygienic significance is about 1 part per million.

ESTIMATION OF OTHER CONTAMINANTS

The all glass absorption system may be used for the collection of acid fumes and vapors (except hydrofluoric acid) using 1% sodium carbonate solution as the absorption medium. The estimation may be by any of the standard chemical procedures for the quantitative determination of anions, but should be direct, rather than by estimation of the unneutralized sodium carbonate. Loss of absorption fluid by mechanical entrainment would introduce a serious error were the indirect method of estimation used.

Methanol in air is estimated by bubbling the air through water using the Aloxite stone absorbers. The estimation is made by oxidation of the methanol to formaldehyde and the estimation of the latter by means of Schiff's reagent (15). The sensitivity of this

determination is about 0.2 mg. of methanol contained in a 25 cc. aliquot or about 10 p.p.m. when 30 liters of air are sampled. Since the maximum allowable concentration for prolonged exposure is usually stated to be 100 p.p.m., this sensitivity is adequate for hygienic surveys.

The other contaminants listed above are similarly absorbed in suitable liquid media and estimated by standard quantitative chemical methods of analysis. All those mentioned have been found adequate for the analysis of industrial air and sufficiently precise to permit a determination of whether or not the environment is hazardous to the health of the employees in the workroom.

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VIII. ESTIMATION OF HALOGENATED HYDROCARBON VAPORS IN AIR

SAMUEL MOSKOWITZ, PH.D. AND WM. J. BURKE, CH.E.

Vapors of halogenated hydrocarbons in air can be determined by the various physical methods used for the general estimation of organic solvents in air. These methods include adsorption on activated charcoal (1) or on silica gel (2), condensation and measurement of the vapor tension of the reevaporated halogenated hydrocarbon (3), use of the interferometer (4), absorption of ultra-violet light (5), and other non-specific methods. Since these methods are non-specific, they cannot be used in the presence of other solvent vapors unless only a total vapor concentration is required.

Trichlorethylene in air has been estimated by absorption in alcohol with subsequent color development by the addition of sodium hydroxide and pyridine (6). Methods for the determination of the concentration in air of methyl chloride (7), methyl bromide (8), and carbon tetrachloride (9) have also been described. Smyth (10) found that the combustion method described by Olsen and his colleagues (9) for carbon tetrachloride in air is also applicable to the estimation of seven other chlorinated aliphatic hydrocarbons and chlorobenzene in air with efficiencies of 98% or higher. Tebbins (11) has adapted the combustion method for the estimation of chlorinated hydrocarbons to field use by making the instrument portable. In this method the halogenated hydrocarbon is burned on a platinum surface in the presence of moist air. The products of combustion are absorbed in a solution of sodium carbonate and sodium arsenite. The hydrogen halide is converted to sodium halide by the sodium carbonate; the free halogen, if any, is reduced to sodium halide by the sodium arsenite. The total sodium halide is then estimated by any suitable standard quantitative procedure, usually volumetric or nephelometric, and the concentration of halogenated hydrocarbon in the air calculated from this result and the volume of air drawn through the combustion tube.

A similar instrument has been used by F. R. Millhiser and W. F. Hemperly for the estimation of chlorinated naphthalenes in air (12). Elkins and his co-workers (13) determine halogenated hydrocarbons by absorption in amyl acetate and then burning the solution in a modified sulphur lamp apparatus.

We use the method described by Tebbins for the estimation of halogenated hydrocarbons with some structural changes. The instrument consists of a wood box, 9½ inches by 11½ inches by 19 inches high (Figure 7). The box contains a rheostat, absorber, drying tube, and flowmeter. Space is provided in the box for the combustion tube and its supporting bracket so that these may be included in the unit for carrying purposes. We prefer operating

the instrument at an air sampling rate of 0.75 liters per minute to prevent undue climbing of the liquid in the absorption tube. Under such operating conditions we have found that the efficiency is 100% (within experimental error) for chlorinated aliphatic hydrocarbons but is only 80% to 85% for alpha-chloronaphthalene. Tebbins reported an efficiency of 98% or over for chlorinated aliphatic hydrocarbons, but only 91% for ortho-dichlorobenzene. Correction factors should be determined for the various halogenated compounds in the air to be tested and applied when significant. The time of sampling varies from 10 minutes to one hour, depending on the concentration of contaminant expected, and the method of analysis depends on the quantity of halogen absorbed.

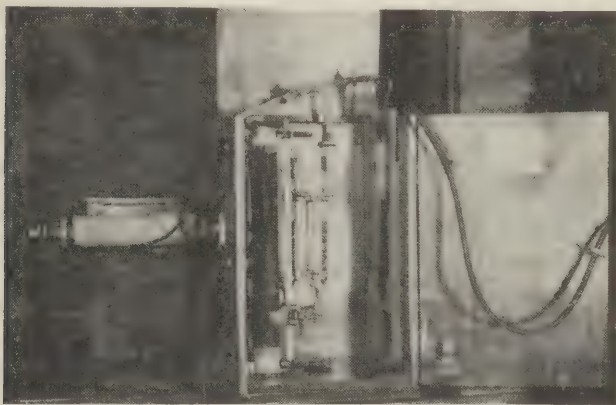


Figure 7.
Combustion Apparatus Assembled for Use

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The photographs used in this series of articles, with the exception of Figures 3 and 4, were prepared by Mr. S. W. Seals.

IX. DETERMINATION OF BENZENE

DETECTION AND ESTIMATION OF BENZENE IN THE PRESENCE OF TOLUENE, XYLENE, AND OTHER SUBSTANCES

B. H. DOLIN, M.A.

The known chemical methods for the determination of benzene do not appear to be applicable in the presence of its homologs, especially toluene and xylene. The sulfuric acid-formaldehyde (4), nickel cyanide (7), dracorubin (2), levulose (10, 11), butanone extraction (13), m-dinitrobenzene reduction (5, 12, 14, 15), and Stepanow colorimetric methods (1) are not specific for benzene. Physical methods for detection of benzene, such as fractionation or ultraviolet absorption (3), likewise cannot be used to estimate the concentration of benzene when it is mixed with unknown concentrations of other substances including its homologs. The method described below was developed in order to satisfy the need (6, 8, 9) of being able to ascertain the presence and concentration of benzene in mixtures of various materials as it is commonly encountered in industry.

Briefly, the method consists of nitration, extraction with ether, development of color with butanone and alkali in alcoholic solution, elimination of the color due to interfering substances by the addition of acetic acid, and comparison of the residual color.

Benzene when nitrated in the manner described below is almost completely converted to m-dinitrobenzene. This compound when treated with butanone and sodium hydroxide in alcoholic solution produces a crimson color. Toluene, when similarly treated, is partly converted to the dinitro compound and forms a blue color which quickly turns violet; xylene forms a relatively permanent

deep blue color. After addition of acetic acid, the color due to benzene remains; the colors due to toluene and xylene disappear rapidly. No color is generated with the aliphatic hydrocarbons and their derivatives such as methanol, ethanol, ethyl acetate, isopropyl alcohol, butanol, butyl acetate, acetone, and similar substances found in such commercial products as paints, lacquers, solvents, and thinners.

REAGENTS AND APPARATUS

Nitrating mixture, equal parts by volume of fuming nitric acid, specific gravity 1.49 to 1.50, and concentrated sulfuric acid, specific gravity 1.84.

Sodium hydroxide aqueous, 1 volume of 40 per cent sodium hydroxide diluted to 4 volumes with distilled water.

Sodium hydroxide alcoholic made by diluting 1 volume of 40 per cent sodium hydroxide to 10 volumes with 95 per cent alcohol and filtering just prior to use.

Acetic acid, made by diluting 1 volume of glacial acetic acid to 10 volumes with 95 per cent alcohol.

Butanone (methyl ethyl ketone), practical grade.

Set of test tubes of about 50-ml. capacity. These tubes should be of the same diameter (2 cm.) and equal transparency. A photo-electric colorimeter may be used if available.

Pipets graduated to 0.01 ml.

PROCEDURE

A 0.50-ml. portion of the solution to be analyzed is measured into a 50-ml. Erlenmeyer flask. The flask is placed in a freezing mixture which consists of chopped ice and salt at a temperature of 0° to -5° C. Nitrating mixture from a buret is added to the solution at the rate of 2 drops per second while the flask is rotated. After 10 ml. have been added, the flask and contents are removed from the ice mixture and 35 ml. of distilled water are added.

The resulting mixture is cooled to room temperature and the nitrated hydrocarbons are extracted with ether, by shaking the mixture with 25-ml. of ether in a 125-ml. separatory funnel and repeating the extraction of the aqueous layer three times with 10-ml. of ether each. The ether layers are transferred into a 100-ml. volumetric flask. The combined ether solutions are poured into the separatory funnel and washed with 10 ml. of aqueous sodium hydroxide reagent, then consecutively with 2 portions of 10 ml. of distilled water. The washed ether solution is then returned to the 100-ml. flask and 95 per cent ethyl alcohol is added to make a total volume of 100 ml. A 10-ml. aliquot of this solution is pipetted into a 50-ml. volumetric flask and 95 per cent alcohol added to the 50-ml. mark.

A 10-ml. portion of the last solution is now measured into one of a set of similar glass tubes. One or more 10-ml. samples of known concentrations of nitrated benzene made as above are also measured into other tubes of the set. To each are added 1.0 ml. of butanone

and 0.50 ml. of alcoholic sodium hydroxide reagent. The tubes are agitated and after 5 minutes the colors are observed. Portions of 0.50 ml. of acetic acid reagent are now added to each tube. The tubes are again agitated and after 10 minutes the color is compared with that of the standard most closely approaching it in intensity.

The comparison may be made as follows: A measured quantity of alcohol is added from a buret or pipet to the solution of greater intensity until both tubes match exactly. If the test solution has a yellow tinge, as is found when high concentrations of xylene are encountered, a dilute solution of sodium or potassium dichromate placed in back of the tube containing the known concentration is of considerable aid in matching the two solutions. The quantity of alcohol added must be taken into consideration. If after 2.5 ml. of alcohol have been added to the test solution, it matches the standard containing the equivalent of 10 per cent benzene, the concentration of benzene in the sample = $\frac{12+2.5}{12} \times 10 = 12.1\%$.

As an alternative to the above, which may be called the dilution method of comparison, a set of standards of varying concentrations may be used. This is known as the standards method of comparison. Standards—e. g., 12.0, 12.5, 13 per cent, etc.—may be obtained from 15 or 20 per cent benzene by diluting the alcoholic solution of nitrated benzene with requisite volumes of alcohol. Butanone, sodium hydroxide, and acetic acid reagents must be added to these standards at the same time and under the same conditions as in the case of the solution whose benzene concentration is to be determined.

The intensity of color may be compared with the aid of an appropriate colorimeter such as the Evelyn photoelectric colorimeter with filter No. 620. Readings are taken on the galvanometer scale 5 minutes after the sodium hydroxide reagent has been added (A), and again 10 minutes after the acetic acid reagent has been added (B). The concentration of benzene is then read directly on a curve previously plotted as concentration of benzene vs. light transmittance or readings on the galvanometer scale. If the difference in the two readings—i.e., B—A—is not very great, no correction is necessary. If, however, the difference is considerable, an empirically obtained correction is applied. If the reading A is 0, the color should be developed on a more dilute solution. This may be obtained by taking a smaller volume of alcohol—ether solution—e. g., 5 ml. instead of 10 ml.—and adding alcohol to a final volume of 10 ml. in the test tube before adding the alkali and acid reagents. This dilution must, of course, be taken into account in the computation.

The reference curve which is used with the photoelectric colorimeter is plotted from the readings obtained on solutions of varying known concentrations of benzene. These solutions are prepared by diluting c.p. benzene with purified petroleum naphtha and treating them in the manner described above and under similar conditions.

The analysis need not take more than 30 minutes. The nitration takes about 2 minutes. The dilution, cooling, extraction, and washing usually consume about 10 minutes, since the stratification of the ether and aqueous layers is prompt. Little more than 15 minutes is required for the production of color and the procurement of the necessary data when the photoelectric colorimeter is used. In the absence of a colorimeter, the additional time consumed in the use of standards is short. Once prepared, the standard solutions keep well when guarded from solvent evaporation by the use of glass-stoppered flasks. They can be used for numerous analyses, since the withdrawal of only 10 ml. is required for a determination.

The curves in Figure 1, as well as in Figures 2 and 3, represent data obtained by measuring with the aid of a photoelectric colorimeter (Evelyn with filter No. 620) the intensity of color developed by the procedure described above. All readings were taken at temperatures $24.5^{\circ}\text{C} \pm 0.4^{\circ}\text{C}$.

Curves 2, 3, 4, 5, and 7, when representing solutions in alkaline media (broken lines, 5 to 15 minutes after sodium hydroxide reagent, but no acid, had been added) do not reach their maxima within 15 minutes. Curves 6 and 8 reach their maxima shortly before 5 minutes. However, the rate of color development which is represented by the ordinates of light transmittance is considerably decreased at the end of the 5-minute period. The rate of color deterioration in the acid media is sufficiently low 10 minutes after the acid has been added, or at a total of 15 minutes after color development was started, to require no additional delay for taking final readings.

Curve 1 in Figure 1 represents results obtained with 10 ml. of a

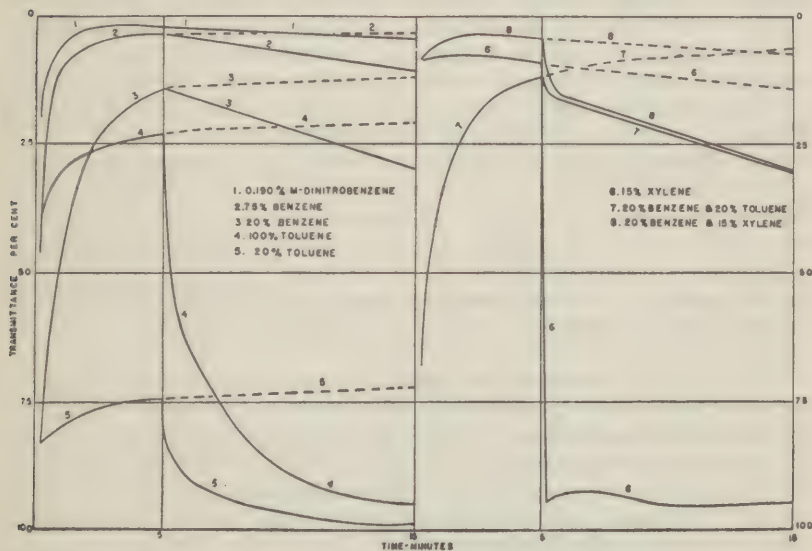


Figure 1. Rate of Color Development and Deterioration

solution of 0.190 gram of Eastman Kodak m-dinitrobenzene in 100 ml. of solution of 95 per cent U.S.P. ethyl alcohol. Curve 2 was derived from a solution prepared by nitrating 0.50 ml. of c.p. benzene, then adding 2.5 ml. of alcohol to 7.5 ml. of its thousand-fold diluted alcoholic solution and treating it with butanone, alkali, and acid, as prescribed. This solution contains an equivalent of 75 per cent of benzene. Curve 3 was drawn from data obtained on a solution composed of 20 volumes of c.p. benzene diluted to 100 volumes with purified petroleum naphtha. Curve 5 was obtained by similar treatment of toluene. Purified petroleum naphtha, in all cases, was prepared by shaking commercial petroleum naphtha and benzene with 100 per cent sulfuric acid to remove aromatic hydrocarbons. The oil was then washed with distilled water, dried with anhydrous potassium carbonate, and distilled. Curve 6 was plotted with data from 15 per cent of xylene in purified petroleum naphtha. Curves 7 and 8 were furnished, respectively, by solutions containing 20 per cent benzene plus 20 per cent toluene, and 20 per cent benzene plus 15 per cent xylene in purified petroleum naphtha. In this paper per cent specified is by volume, unless otherwise stated.

The rate of color development of benzene, when treated by the above procedure, is rapid at first, then gradually diminishes. After addition of the acid reagent the color remains the same, though decreased somewhat in intensity (curves 2 and 3, Figure 1.) The color formed with the solution of m-dinitrobenzene which corresponds in concentration to that given by 100 per cent benzene, if completely nitrated to m-dinitrobenzene, shows the same characteristics (curve 1, Figure 1). In contrast, the color of the toluene complex develops slowly, does not reach the intensity produced by equal concentrations of benzene, and fades rapidly after adding the acid reagent (curves 4 and 5). Xylene, at a 15 per cent concentration, almost instantaneously exhibits a color nearly as intense as 75 per cent benzene. However, 15 seconds after adding the acid reagent, its blue color completely disappeared (curve 6).

The slight interference resulting from the presence of toluene and xylene is illustrated by curves 7 and 8 in Figure 1. In alkaline media, both curves differ considerably from curve 3, although they all contain 20 percent benzene. After the acid reagent is added, all curves rapidly assume the form given by 20 per cent benzene despite the fact that one solution contains 20 per cent of toluene and another 15 per cent of xylene in addition to 20 per cent of benzene.

Varying concentrations of benzene, toluene, and xylene produce different colors and intensities of color when alkali reagent is added to the alcoholic solutions of butanone and the nitrated compounds. The contrast between benzene on one hand and toluene and xylene on the other becomes much more pronounced after the acetic acid reagent is added. This is illustrated in Figure 2. The broken lines here present results 5 minutes after the sodium hydroxide reagent had been added. The solid lines represent results obtained 10

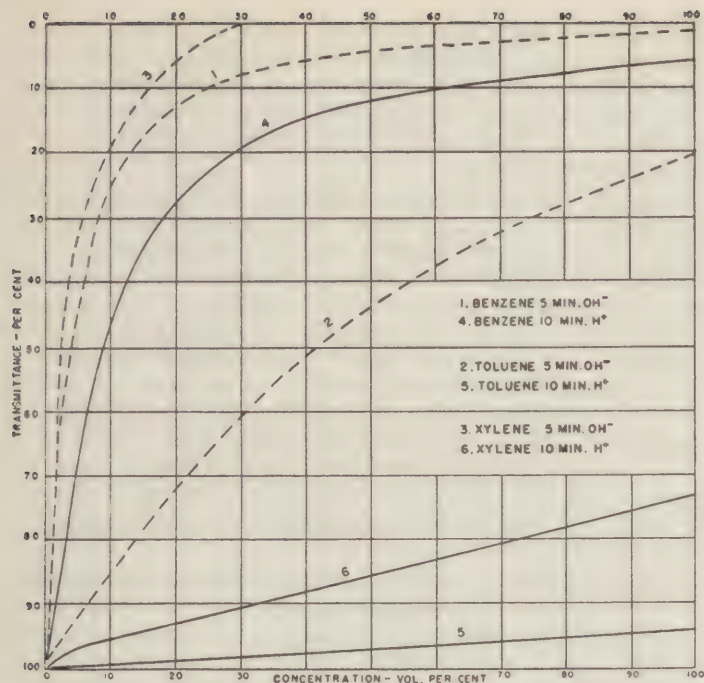


Figure 2. Relationship of Concentration To Intensity of Color

minutes after the acetic acid reagent had been added or a total of 15 minutes after color development had begun. Curves 1 and 3 demonstrate the resemblance of the xylene to the benzene reaction when in alkaline media. This resemblance is practically nullified 10 minutes after the acetic acid has been added. Benzene largely retains its properties—i.e., of an exponential curve $y = ae^{-kx}$ (curve 4, Figure 2)—whereas the curves for toluene and xylene are transformed into straight lines located at the lower section of the graph.

The concentration of either toluene or xylene can also be determined by this method, provided only one of these and no benzene or other chromogenic compound is present. Better results, however, in this case are obtained when the color comparison is made 5 minutes after the sodium hydroxide reagent has been added, and the broken line curves in Figure 2 are used.

Mixtures of these compounds can thus also be qualitatively ascertained. A solution of benzene and toluene gives a purplish violet color, whereas a solution of benzene and xylene gives an opaque violet color. After addition of the acid reagent the crimson color gradually appears in the case of benzene and toluene, whereas it almost immediately emerges in the case of benzene and xylene solutions. On observation with the unaided eye, the intensity of color

indicates the concentration of chromogen. When the photoelectric colorimeter is used, wide differences between the 5- and 15-minute readings indicate high concentrations of either toluene or xylene or both. The character and position of a curve plotted as light transmittance vs. time will indicate the concentration of either toluene or xylene or both.

Curve 4 of Figure 2 is the reference curve mentioned under Procedure above. Figure 3 shows this curve broken up in four sections plotted on three different scales for the abscissa. This was necessitated by the fact that the constants a and k of the curve $y = ae^{-kx}$ are applicable for limited sections of the curve. The formula $y = mx + b$ or a straight-line function, actually describes some sections of the curve best. Furthermore, the use of the curves in Figure 3 facilitates readings of benzene concentrations with an error no greater than the maximum error inherent in the manipulations. The complete curve is shown at the lower right corner of the graph. The complete curve obtained from similar treatment of c.p. toluene was inserted here for comparison. In view of the fact that the benzene curve rises very sharply—i.e., the

TABLE I. DETERMINATION OF BENZENE BY DILUTION METHOD OF COMPARISON

| Composition of Samples | | | | | Benzene Found Vol. % | Error Vol. % | Error % |
|------------------------------|---------|-------------------|--------------------|-------|----------------------------|-----------------|------------|
| Sample No. | Benzene | Toluene Volume | Xylene per cent | Other | | | |
| 1 | 75.0 | 25.0 | .. | .. | 77.0 | 2.0 | 2.7 |
| 2 | 50.0 | 20.0 | 30.0 | .. | 50.8 | 0.8 | 1.6 |
| 3 | 40.0 | 60.0 | .. | .. | 39.8 | -0.2 | 0.5 |
| 4 | 30.0 | 70.0 | .. | .. | 30.7 | 0.7 | 2.3 |
| Petroleum naphtha | | | | | | | |
| 5 | 25.0 | 25.0 | 25.0 | 25.0 | 24.8 | -0.2 | 0.8 |
| 6 | 20.0 | .. | 80.0 | .. | 19.7 | -0.3 | 1.5 |
| 7 | 10.0 | 90.0 | .. | .. | 10.0 | 0.0 | 0.0 |
| 8 | 5.00 | 95.0 | .. | .. | 5.00 | 0.0 | 0.0 |
| 9 | 1.00 | .. | .. | 99.0 | 1.00 | 0.0 | 0.0 |
| Butyl acetate | | | | | | | |
| 10 | 1.00 | 10.0 | 69.0 | 20.0 | 1.04 | 0.04 | 4.0 |
| 11 | 0.25 | .. | .. | 52.50 | 0.24 | -0.01 | 4.0 |
| Ethyl acetate 25.85 | | | | | | | |
| Isobutyl alcohol 21.40 | | | | | | | |
| Petroleum naphtha | | | | | | | |
| 12 | 0.20 | .. | .. | 99.80 | 0.19 | -0.01 | 5.0 |

TABLE II. DETERMINATION OF BENZENE BY STANDARDS
METHOD OF COMPARISON

| (Standards used: equivalent of 1 to 10% benzene by volume) | | | | | | | | |
|--|---------|----------------|-----------------|-------------------|----------------------|--------------|---------|--|
| Composition of Samples | | | | | | | | |
| Sample No. | Benbene | Toluene Volume | Xylene per cent | Petroleum naphtha | Benzene Found Vol. % | Error Vol. % | Error % | |
| 1 ^a | 50.0 | 50.0 | .. | .. | 50.0 | 0.0 | 0.0 | |
| 2 ^a | 40.0 | 60.0 | .. | .. | 39.0 | -1.0 | 2.5 | |
| 3 ^a | 30.0 | .. | 70.0 | .. | 31.0 | 1.0 | 3.3 | |
| 4 ^a | 20.0 | .. | 80.0 | .. | 20.0 | 0.0 | 0.0 | |
| 5 | 10.0 | 90.0 | .. | .. | 10.0 | 0.0 | 0.0 | |
| 6 | 10.0 | .. | .. | 90.0 | 9.9 | -0.1 | 1.0 | |
| 7 | 5.00 | 95.0 | .. | .. | 5.0 | 0.0 | 0.0 | |
| 8 | 3.00 | .. | 97.0 | .. | 2.9 | -0.1 | 3.3 | |
| 9 | 2.00 | 98.0 | .. | .. | 2.0 | 0.0 | 0.0 | |
| 10 | 1.00 | 99.0 | .. | .. | 1.0 | 0.0 | 0.0 | |
| 11 | 1.00 | 99.0 | .. | .. | 1.05 | 0.05 | 5.0 | |

^a Diluted 10 times with alcohol before comparison.

difference in color intensity for a given increment of benzene is greater—from 0.01 to 30 per cent of benzene this range was plotted in the form of three different curves. The section for 25 to 100 per cent of benzene was plotted on a fourth curve to a scale coarser than that of curves 3, 2, and 1, but finer than the similar curve in Figure 2.

CHECKING OF METHOD

In order to ascertain the accuracy of the method, solutions containing different concentrations of benzene and other substances were prepared. The results obtained are shown in Tables I to IV.

The standards used for visual comparison of the test solutions in Table I were those corresponding to 0.2, 1.0, 5.0, 10.0, 20.0, and 50.0 per cent benzene. The standard used in each case was that most closely approaching in color the test solution. In the case of Nos. 1, 2, 4, 5, 9 and 11 a small quantity of alcohol gradually added to the test solution produced a color that matched the standard. Alcohol greater than this quantity reduced the intensity

of color. The formula used in these cases was $B = \frac{12 + a}{12} S$,

where B = volume per cent of benzene, S = benzene concentration of standard used, and a = ml. of alcohol added to match the color of the standard solution. In the case of Nos. 3, 6, and 12 the standards had to be diluted. The formula used in the latter

case was $B = \frac{12}{12 + a} S$.

Table II illustrates the results obtained with test solutions compared by the alternative visual method of standards comparison. A series of standards corresponding to the range of 1 to 10 per

TABLE III. DETERMINATION OF BENZENE WITH PHOTOELECTRIC COLORIMETER

| Sample No. | Composition of Samples | | | | | Benzene Found | | | |
|------------|------------------------|---------|--------|-------------------|------------------|------------------|------------------|-----------------|-----------------|
| | Benzene | Toluene | Xylene | Petroleum Naphtha | Other | As read on curve | Corrected—Volume | Error per cent— | Error per cent— |
| 1 | 75.0 | 25.0 | ... | ... | ... | 75.3 | ... | 0.3 | 0.4 |
| 2 | 50.0 | ... | ... | 50.0 | ... | 50.2 | ... | 0.2 | 0.4 |
| | | | | | Butyl acetate | | | | |
| 3 | 5.00 | 40.0 | 10.0 | 5.00 | 40.0 | 5.08 | 4.99 | -0.01 | 0.2 |
| 4 | 2.00 | 50.00 | 48.0 | ... | ... | 2.29 | 2.01 | 0.01 | 0.5 |
| 5 | 1.00 | 99.0 | ... | ... | ... | 1.12 | 0.99 | -0.01 | 1.0 |
| 6 | 0.250 | ... | ... | ... | 52.5 | 0.25 | ... | 0.00 | 0.0 |
| | | | | | Ethyl acetate | | | | |
| | | | | | 25.85 | | | | |
| | | | | | Isobutyl alcohol | | | | |
| | | | | | 21.4 | | | | |
| 7 | 0.050 | ... | ... | 80.0 | 4.28 | 0.065 | 0.055 | 0.005 | 10.0 |
| | | | | | Butyl acetate | | | | |
| | | | | | 10.50 | | | | |
| | | | | | Ethyl acetate | | | | |
| | | | | | 5.17 | | | | |
| 8 | 0.010 | 0.06 | 0.03 | 81.9 | 4.00 | 0.030 | 0.020 | 0.01 | 100.0 |
| | | | | | Butyl acetate | | | | |
| | | | | | 5.00 | | | | |
| | | | | | Isobutyl alcohol | | | | |
| | | | | | 4.00 | | | | |
| | | | | | Acetone | | | | |
| | | | | | 5.00 | | | | |

cent benzene with unit intervals was first used. The color was then reproduced simultaneously with several standards of concentrations with increments corresponding to 0.1 per cent of benzene varying from the standard most closely matching the test solution. Whenever the concentration of the test solution appeared to be greater than 10 per cent benzene, the test solution was diluted tenfold with alcohol, the color redeveloped, and the comparison repeated.

The determinations listed in Tables III and IV were made with the aid of the graph in Figure 3. The errors found when differences in readings between the 5- and 15-minute intervals were considerable were greatly minimized by the use of empirically derived corrections. The correction applied in Table IV as well as the final results was multiplied by 10, since the test solutions were diluted tenfold. The formula used in computation for the series in Table III was $\text{benzene \%} = C - (B - A - 25) 0.005$; the formula used for the series in Table IV was $\text{benzene \%} = 10(C - (B - A - 25) 0.005)$. C is benzene per cent corresponding to reading B on galvanometers. B and A are as given under Procedure.

ACCURACY AND SENSITIVITY

The presence of petroleum naphtha, ethyl acetate, butyl acetate, isobutyl alcohol, acetone, toluene, and xylene did not interfere with the determinations of benzene in the experiments tabulated. Reasonable accuracy, with a mean error of 1.6 per cent, was attained when the intensity of color produced was matched without the aid of a colorimeter. Greater accuracy was attained with the aid of a photoelectric colorimeter where a mean error of 0.9 per cent for a similar range of concentrations was in evidence. Concentrations less than 0.2 per cent benzene could not be determined with the naked eye, whereas concentrations down to 0.01 per cent benzene could be determined by the use of a photoelectric colorimeter. The errors involved at concentrations less than 0.2 per cent benzene, however, were considerable and amounted to 10 per cent at 0.05 per cent benzene and more at lower concentrations.

The 10-ml. aliquot of solution used for color development represents 0.01 ml. of the sample of 0.50 ml. taken for analysis and diluted to 100 X 5. Since 0.01 per cent benzene can be detected, the method appears to be sensitive to 1×10^{-6} ml. or 8.8×10^{-7} g. of benzene. By visual comparison, in the absence of a photoelectric colorimeter or when an error above 1 per cent is not permissible, the sensitivity is reduced to 2×10^{-5} ml. or 1.8×10^{-5} g. of benzene.

The concentration of benzene vapor in air may be determined by the above method after the vapor has been transformed from the gaseous to the liquid phase. This may be accomplished by adsorbing or dissolving the vapor in petroleum naphtha or alcohol. The concentration of benzene in the resulting solution may then be determined as prescribed. Without diluting the ether extract, but using the total nitrated material in alcoholic solution, 8.8×10^{-7} g. or 0.27 p.p.m. may be detected on a sample of 1 liter of air. Concentrations of 1.8×10^{-5} g. per liter of air or 5.6 p.p.m. may be determined with an error less than 1%. By sampling 10 ml.

TABLE IV. DETERMINATION OF BENZENE WITH PHOTOELECTRIC COLORIMETER

| Sample No. | Benzene | Dilution X 10 (10,000 total) | | | | | Benzene Found As read on curve | Corrected Volume | Error per cent— | Error per cent— |
|---------------|---------|------------------------------|----------|---------|-------|-------|--------------------------------------|---------------------|--------------------|--------------------|
| | | Composition of Samples | | | | | | | | |
| | | Petroleum | | | | | | | | |
| | | Toluene | Xylene | Naphtha | Other | | | | | |
| | | Vol. | per cent | | | | | | | |
| 1 | 75.0 | 25.0 | ... | ... | ... | 7.49 | 74.9 | —0.10 | 0.1 | |
| 2 | 50.0 | 20.0 | 30.0 | ... | ... | 5.16 | 50.1 | 0.10 | 0.2 | |
| 3 | 25.0 | 25.0 | 25.0 | 25.0 | ... | 2.67 | 24.9 | —0.10 | 0.4 | |
| Acetone | | | | | | | | | | |
| 4 | 20.0 | ... | ... | ... | 80.0 | 2.03 | 20.3 | 0.30 | 1.5 | |
| 5 | 20.0 | 40.0 | 20.0 | 20.0 | ... | 2.19 | 19.8 | —0.20 | 1.0 | |
| 6 | 10.0 | 90.0 | ... | ... | ... | 1.00 | 10.0 | 0.00 | 0.0 | |
| 7 | 10.0 | ... | 90.0 | ... | ... | 1.21 | 9.70 | —0.30 | 3.0 | |
| 8 | 1.00 | 85.0 | 14.0 | ... | ... | 0.305 | 1.05 | 0.05 | 5.0 | |
| Butyl acetate | | | | | | | | | | |
| 9 | 1.00 | 50.0 | 10.0 | 9.00 | 30 | 0.250 | 1.00 | 0.00 | 0.0 | |

portions of air, concentrations down to as low as 8.8×10^{-5} g. of benzene per liter of air or 27 p.p.m. should be possible of detection. The significance of this may be realized when it is perceived that numerous samples of air may be taken in a comparatively short time and that many small portable containers may be used.

SOURCES OF ERROR

The products formed on treating benzene with nitrosulfuric acid depend not only on the volume of acid used and the temperature surrounding the solution but also on the rate of adding the acid. The heat formed in the reaction must be allowed sufficient time to dissipate. Too rapid addition of the nitrating acid tends to form undesirable by-products with a lower yield of m-dinitrobenzene.

m-Dinitrobenzene is soluble in ether to the extent of 6.7 grams per 100 ml. at 15° C. It is soluble in water to the extent of 0.047 gram per 100 ml. at 15° C. Although most of the nitrated compound enters the ether layer on extraction, some of it tends to remain in the aqueous layer. The favorable distribution of m-dinitrobenzene between ether and water is probably adversely affected by the mutual miscibility of the two solvents. However, even with this effect, a single extraction might be sufficient were it possible to separate the two phases completely. To ensure reasonably complete extraction, four ether extractions are made, and only small volumes of water are used to wash the ether extract.

Increase in temperature, as is often the case in chemical reactions, hastens the production of color in alkaline media and the disappearance of color in the acid media in the case of the dinitrobenzene as well as the nitrated toluene and xylene. Light also has some effect on the rate of color development and deterioration. The temperature should be within 0.4° C., and light conditions and the time elapsed should all be the same when the readings are taken with the photoelectric colorimeter as when the reference curve was prepared. When the color is compared by visual inspection, the unknown and standard are subjected to the same conditions and the effect is the same on all solutions. A series of permanent standards made from dyes or inorganic salts is not recommended because this would be applicable for only one given set of conditions.

The sensitivity of the individual observer to fine gradations of color and color intensity will influence the magnitude of error resulting from visual color comparison. This personal error, which inevitably accompanies all colorimetric determinations, may be eliminated by the use of the photoelectric colorimeter.

The photoelectric colorimetric determinations listed in Tables I and II show mean errors of 0.4 and 1.2 per cent respectively, for concentrations above 0.2 per cent of benzene. The lower apparent accuracy in Table II is not due so much to the added manipulation of additional dilution as to the resultant decrease in benzene concentration of the test solutions. This dilution, necessitated by the fact that the solutions tested developed too intense a color in the

X 1000 dilution, may perhaps be obviated by the substitution of a more appropriate filter than that used in the above experiments.

Since the galvanometer scale used can be read only to the nearest 0.25 division, the accuracy of the apparatus is limited in the presence of very high or very low concentrations of chromogen. The probability of an error of 2 per cent in 95 per cent benzene, for example, is high, even if all precautions are carefully taken. In the case of high transmittance or low concentrations of benzene, an experimental error of the magnitude of 0.005 per cent may produce an error of 10 per cent in material containing 0.05 per cent benzene. It would thus seem advisable to read the concentration of benzene at light transmittance between 20 and 80 per cent in order to avoid the upper and lower extremes of the reference curve. This may be attained by adjusting the dilution of the test solution after a preliminary determination.

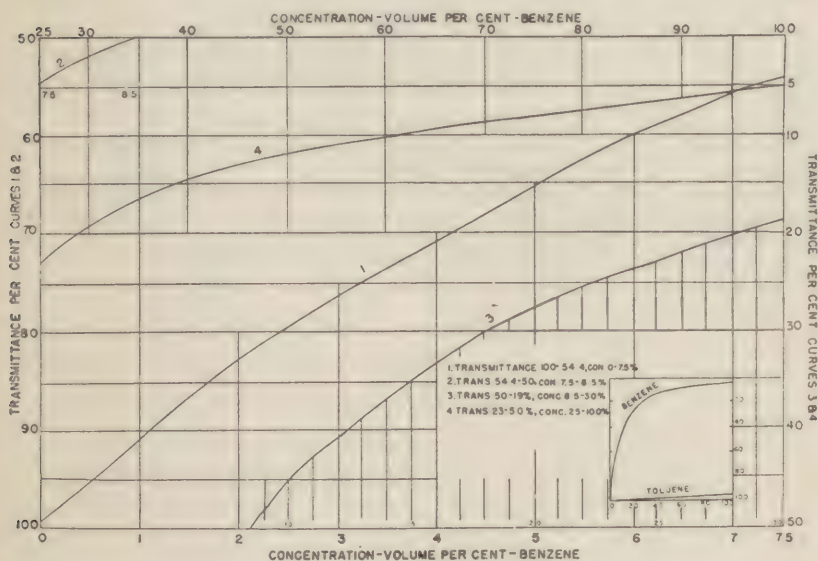


Figure 3. Reference Curve For Photoelectric Colorimeter

SUMMARY

A method developed for the estimation of benzene in the presence of toluene, xylene, and other substances requires little material for analysis, is rapid, and is sensitive to 8.8×10^{-7} g. of benzene.

Concentrations varying from 0.25 to 75 per cent of benzene by volume have been determined with a mean error of 0.9 per cent.

The method may be used for the determination of small air samples.

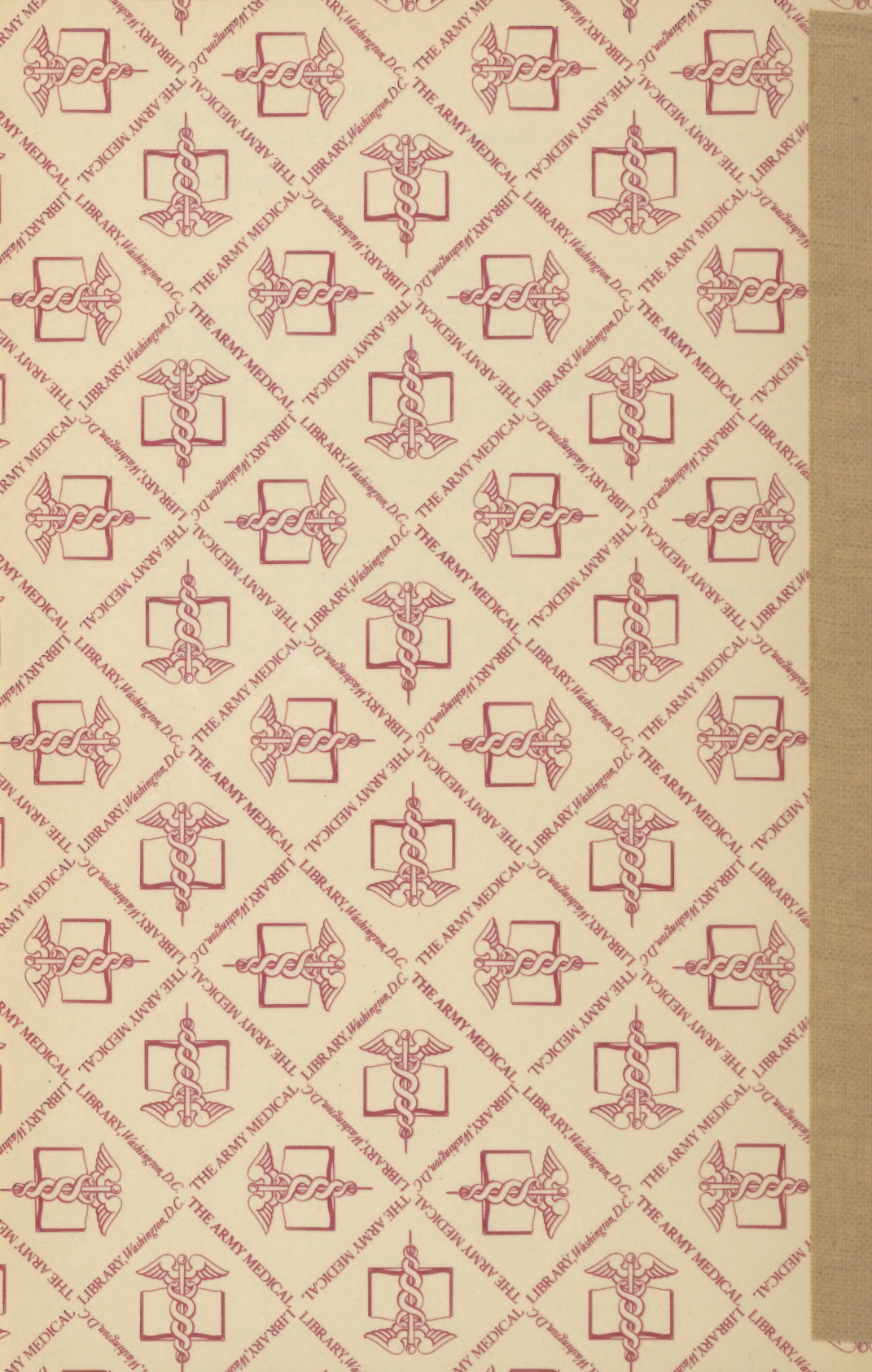


Means for the identification of toluene, xylene, and benzene have been given.

The accuracy of the method, the sources of error, and the precautions to be taken in order to minimize the effect of the errors are discussed.

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